OPEN-BED SOIL PLANAR CHROMATOGRAPHY FOR IDENTIFICATION AND SEPARATION OF AGROCHEMICALS

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF

Master of Philosophy

IN

APPLIED CHEMISTRY

By

SABA HABIB

DEPARTMENT OF APPLIED CHEMISTRY
Z.H. COLLEGE OF ENGINEERING & TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)

2008

Dedicated

to

My Beloved Parents

Certificate

This is to certify that the work incorporated in this thesis entitled "Open-Bed Soil Planar Chromatography for Identification and Separation of Agrochemicals" being submitted by Miss Saba Habib is in partial fulfillment of the requirements for the award of the degree of Master of Philosophy in Applied Chemistry of Aligarh Muslim University, Aligarh.

The work embodied in this thesis is original and bonafide record of the research carried out under my supervision.

31/01/08

(Dr. Ali Mohammad)
Supervisor

Acknowledgements

There are a number of people without whose support and cooperation the completion of my dissertation would not have been possible. First and foremost I would like to express my deepest gratitude to my supervisor Dr. Ali Mohammad, Reader and Chairman, Department of Applied Chemistry. His keen research acumen, vast knowledge, and great patience enabled in understanding the fascinating field of Thin-Layer Chromatography. Throughout my thesis writing period, Dr. Mohammad has provided much needed encouragement, inspiration, sound advice, and good sense of humor. I firmly believe that this thesis would not have seen the light of day without Dr. Mohammad's support and wise counsel.

I would like to extend my sincere thanks to my friends and lab colleagues who were always there for me whether for providing personal support or critiquing my work. Here is a list in no particular order: Hina aapa, Moheman bhai, Showkat bhai, Rubi aapa, Almas aapa, Nazrul bhai, Shumaila aapa, Nazia, Sameen, Kashif and Sudhanshu. I would like to take this opportunity to thank Mr. Farooq Hassan for his thoughtfulness and care in typing this dissertation.

I wish to thank all my family members for providing encouragement, care, support, and a loving environment. Their support and encouragement meant a lot to me and helped me bring out the best in me. I can't miss mentioning my cute little niece Anam, who always brought a smile on my face, even in somewhat tense moments while writing this dissertation.

Last but not least, I wish to thank my parents – they bore me, raised me, supported me, taught me, and loved me. I would have been nowhere without them and it is to them that I dedicate this thesis.

I would be failing in my duty if I do not mention my firm belief in Almighty Allah. He was with me at every moment during my thesis writing process and otherwise.

Saba Habib

(SABA HABIB)

CONTENTS

Chapter – 1

General Introduction

GENERAL INTRODUCTION

1.1 Introduction

Chromatography is a physical method of separation, in which two or more components to be separated are distributed between two phases, one of these phases constituting a stationary bed of large surface area, the other being a fluid that percolates through or along a stationary bed. Chromatography is a powerful separation method that finds application to all branches of science. It is an excellent technique for the separation and analysis of highly complex mixtures. The chronological development in separation techniques of chromatography is presented in Table 1.1.

Table: 1.1 Chronological Development of Chromatographic Techniques

S. No.	Technique	Year of Discovery	Discoverer
1.	Thin-layer chromatography (TLC) (adsorption)	1938	Izmailov and Schraiber
2.	Partition chromatography	1941	Martin and Synge
3.	Paper chromatography (PC)	1944	Consden, Gordan and Martin
4.	Counter current distribution (CCD)	1944	Craig
5.	Gel-permeation chromatography (GPC)	1945	Barrer
6.	Gas chromatography (GC)	1946	Claesson
7.	Ion-exchange chromatography (partition)	1947	Meyer and Thompkins
8.	Electrophoresis	1948	Haugaard and Kroner
9.	Thin-layer chromatography (TLC) (partition)	1951	Kirchner, Miller and Keller

10.	Gas liquid chromatography	1952	James and Martin
11.	High-performance liquid chromatography (HPLC)	1952	James and Martin
12.	Ion-exchange chromatography (IEC partition)	1963	Samuelson
13.	High performance thin layer chromatography (HPTLC)	1974	James and Martin
14.	Ion chromatography	1975	Small, Stevens and Baumman
15.	Over pressured layer chromatography (OPLC)	1979	Tyihak, Minescovics and Kalasz

1.2 CLASSIFICATION OF CHROMATOGRAPHIC METHODS

The chromatographic systems can be classified according to (a) state of aggregation of phases, (b) physical arrangement of the phases and (c) mechanism underlying the distribution equilibrium. Chromatographic systems generating from solid, liquid and gaseous phases are (a) liquid-liquid (b) liquid-solid (c) gas-liquid and (d) gas-solid.

According to the latest nomenclature for chromatography [1] all chromatographic methods can be separated into column chromatography and planar chromatography, depending upon the shape of the chromatographic bed.

The classification of chromatographic techniques has been illustrated in Fig.1

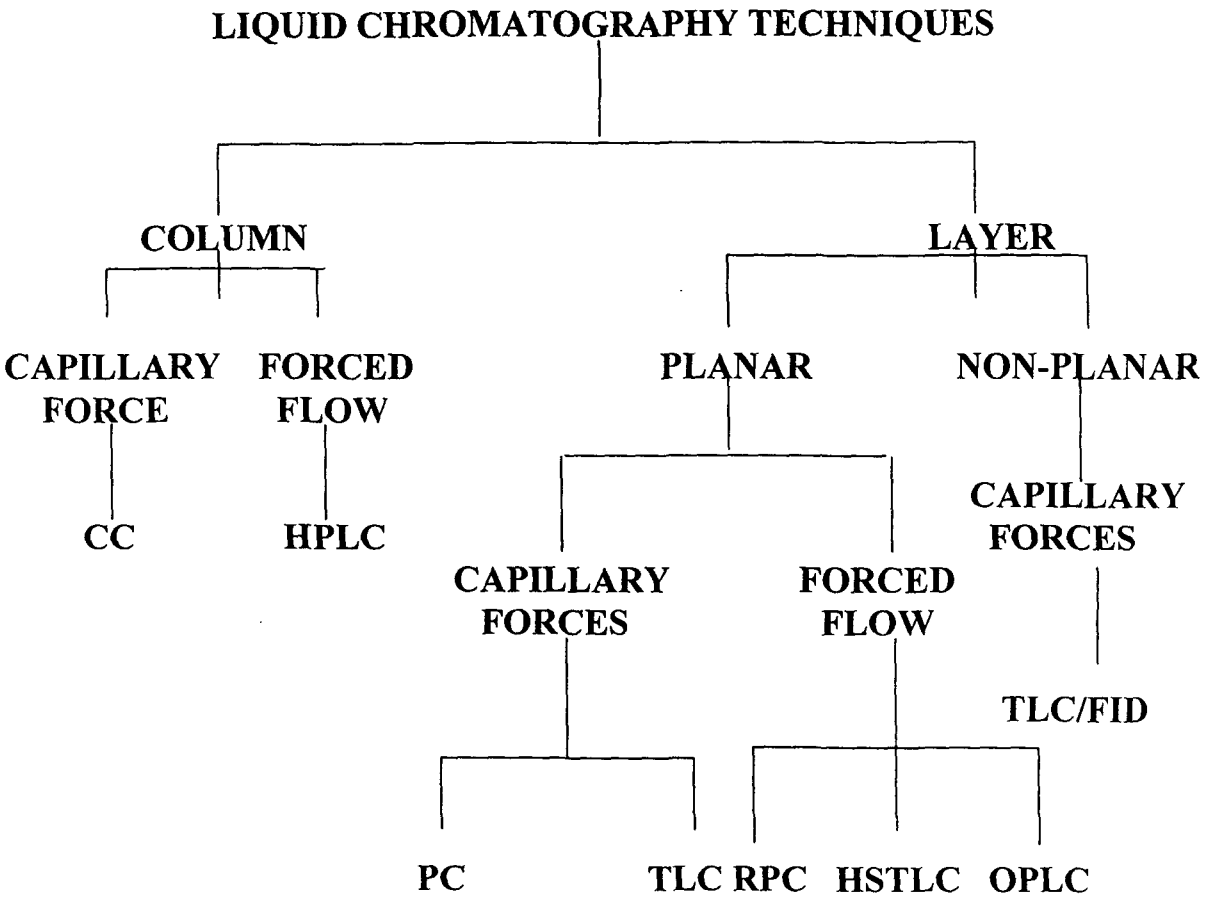

Fig. 1. Classification of liquid chromatographic techniques according to the physical arrangement of the phases.

Note: CC = Column chromatography, HPLC = High pressure liquid chromatography, PC = Paper chromatography, TLC = Thin-Layer chromatography, RPC = Reversed phase Chromatography, HSTLC = High Speed TLC, DPLC = Over Pressure Layer chromatography, FID = Flame Ionization Detector.

Column chromatography is a separation technique in which the stationary bed is within a tube. The particles of the solid stationary phase may fill the whole inside volume of the tube (packed column) or be concentrated on or along the inside tube wall leaving an open unrestricted path for the mobile phase in the middle part of the the tube (open-tubular column).

Planar chromatography is a separation technique in which the stationary phase is present as or on the plane. The plane can be unmodified paper, paper impregnated with a substance as a stationary bed (paper chromatography, PC) or a layer of solid particles spread on a support, eg. glass plate (thin layer chromatography, TLC). Sometimes planar chromatography is also termed 'Open-bed chromatography' (1). In Table 1.2, comparative analysis of planar and non-planar chromatography has been illustrated, which underlines the similarities of the important chromatographic variants and the differences between them.

Table 1.2. Comparision of planar and nonplanar (column chromatogrphy).

S. No.	Characteristics of the method	Open bed	Planar chromatography closed bed		Non planar (column) chromatography – closed bed	
			Equal time [a]	Equal migration [b]	Equal time [a]	Equal migration [b]
1.	Shape of chromatographic bed	Planar	Planar	Planar	Cylinder	Cylinder
2.	Arrangement of the zones after separation	Within the bed	Within the bed	In the flow of mobile phase outside the bed	Within the bed	In the flow of mobile phase outside the bed
3.	Retention time	The same for all the compounds chromatographed	The same for all the compounds chromatographed	Different for all the compounds chromatographed	The same for all the compounds chromatographed	Different for all the compounds chromatograhed
4.	Migration of the zone along chromatographic bed	Different for all the compounds chromatographed	Different for all the compounds chromatographed	The same for all the compounds chromatographic	Different for all the compounds chromatographed	The same for all the compounds chromatographed
5.1	Realization of circular and anticircular chromatography realization of	Realized	Realized	Realized	No	No
5.2	Two-dimensional chromatography	Realized	Realized	Possible (under defined conditions)	No	No

(a) Equal-time variant - the retention of all chromatographed compounds is the same, the zones of the separated compounds are located within the chromatographic bed; the migration distances are different.

(b) Equal-migration variant - all separated compounds migrate the same distance, the bed length; the retention times are different.

1.3 HISTORICAL OVERVIEW OF PLANAR CHROMATOGRAPHY

The history of planar chromatography goes back to early work performed by Runge [2, 3], who separated dissolved dyes on filter paper. In addition to his separations, he produced a variety of colours of different composition. Runge is considered the originator of paper chromatography (Weil and Williams [4]). Ettre [5] considers the capillary analysis of Goppelsroeder and pupils to be the closest technique to that known today as planar chromatography. Like Runge, they also separated coloured compounds.

Later Ismailov and Schraiber [6, 7] used alumina particles spread on a glass plate instead of a packed in a column. The thickness of their layer was approximately 2 mm (See Kreuzig [8]). Ismailov and Schraiber used alumina with no binder whereas Meinhard and Hall [9] introduced a starch binder to 'immobilize' the adsorbent on a glass microscope slide. Ettre [4] reports that Meinhard and Hall called their method 'surface chromatography' - a reference to the two dimensional nature of their stationary phase. Ismailov and Schraiber [6, 7] and Meinhard and Hall [9] developed a circular planar chromatogram [5] and Kirchner and Keller [10] introduced the ascending development of silica-impregnated paper strips.

A major impetus to the widespread use of thin-layer chromatography was provided with Stahl [11-13]; he standardizing thin layer chromatography by construction a spreader for preparation of thin-layer plates, suggested the use of silica as adsorbent and edited an excellent text book [13] etc. At that time different arrangements for development, and appropriate chemicals and laboratory supplies for thin layer chromatography became commercially available.

The continuing popularity of planar chromatography is based on features such as possibility of direct observation, use of specific and colorful reactions, and the possibility of two-dimensional separation. Capillary action results in the migration of mobile phase through the stationary phase bed. Since the work summarized in this dissertation is based on thin-layer chromatography (TLC), it is, therefore, necessary to discuss the important features of this technique. The following paragraphs present on overview of all important aspects of this widely popular and versatile separation technique.

1.4 THIN LAYER CHROMATOGRAPHY

Thin-layer chromatography (TLC), a subdivision of liquid chromatography is carried out on a flat surface and hence it is sometimes referred to as planar chromatographic separation technique. In TLC, the mobile phase (a liquid) migrates through the stationary phase (thin layer of porous sorbent on a flat inert surface) by capillary action. This technique is simple, versatile and inexpensive means of separating and identifying the components of complex mixtures of inorganic, organic and biochemical substances.

The beginning of TLC can be ascribed to the report of Dutch biologist, Beyerink [15], who separated hydrochloric and sulfuric acids in the form of fine rings on thin layer of gelatin using a visualizing agent. Following the same method, Wijsman [16] identified the presence of two enzymes in malt diastase using a fluorescent method for detecting separated enzymes on thin layer. He used the bacteria obtained from sea water as fluorescent agent. However, the invention of TLC is usually credited to two Russian scientists, N. A. Ismailov and M. S. Schraiber, who used binder free horizontal thin layer (2mm thick) of alumina spread on glass plate to the analysis of pharmaceutical preparations which led to the publication of their classical paper [6] on "A Spot Chromatographic Method of Analysis and its

Application in Pharmacy" in 1938. Since their method consists of depositing a drop of sample solution being investigated and the development by the application of several drops of solvent on flat surface of adsorbent before observing the separated zones, it was called "Drop Chromatography or Spot Chromatography". They also pointed out the usefulness of this method for preliminary testing of sorbent properties before their utilization in the form of column. Though Izmailov is best known for his fundamental work on TLC, his main field of interest was electrochemistry for which he received the Mendeleiv Prize of the Academy of Science of USSR in 1961.

In 1939, Brown developed a useful technique called "Circular Paper Chromatography" which involves the placing of filter paper between two glass plates and the application of sample and the developing solvent through a small hole of the upper plate. To obtain stronger adsorbent, he proposed the use of a thin layer of alumina between two sheets of paper. In 1940, Lapp and Erali used a loose layer of alumina spread on a glass slide that was supported on an inclined aluminium sheet. This sheet was cooled at its upper end and heated at the lower end. The sample was placed at the top of the adsorbent layer and gradually developed by solvent descending movement. The use of heat at the lower end of the layer increased the evaporation rate of the solvent so that increased development could take place [17]. It is interesting that, in 1949, two American chemists, Meinhard and Hall [9] gave the concept of "Surface Chromatography" and described their work on the use of microscope slides coated with a mixture of alumina (an adsorbent) and celite (a binder) to separate Fe^{2+} and Zn^{2+}. Their work was probably the first application of TLC for the separation of organic ions.

TLC is the most widely used chromatographic method because of the following reasons (a) The availability of limited number of liquid chromatographs in research laboratories (b) simplicity of the techniques (c)

possibility of simultaneous analysis of a large number of samples (d) low cost and (e) the ease of operation by a researcher with little experience. Numerous publications on TLC applications attest to the versatility and applicability of this technique in all branches of science. It has opened new fields of exploration and become an invaluable aid to separation scientists.

TLC can be used for (a) qualitative analysis (to identify the presence or absence of a particular substance in a mixture) (b) quantitative analysis (to determine precisely and accurately, the amount of a particular substance in a sample mixture) and (c) preparative analysis (to purify and isolate a particular substance for subsequent use). All three cases require the common procedures of sample application, chromatographic separation and sample component visualization. However, analytical TLC differs from preparative TLC as the sample solution or amount is applied on thinner layers in the former case, whereas thicker TLC plates are used for preparative TLC.

1.5 TLC PRODECURE

The TLC process is an off-line process in which all the procedural steps are carried out independently. The basic TLC procedure involves the spotting of the sample mixture (5-10 µl) at about 2 cm above the lower edge of the TLC plate, drying the spot (usually at room temperature), development of plate with suitable mobile phase to a distance of 8-10 cm inside a cylindrical or rectangular closed chamber by ascending technique, withdrawing plate from the developing chamber, drying the layer at room temperature to remove the mobile phase, detection of spots on TLC plate using suitable detection reagent, measurement of R_F values of the resolved spots and the quantitative estimation of the analyte after extraction from the layer with suitable extractant. The differential migration of components results due to varying degrees of affinity of the components in a mixture for stationary and mobile phases.

Sample Preparation

Standard methods for sample preparation, identification and separation of analyte present in a variety of samples such as plants, food, biological, geological and environmental samples have been reported. In general, solutions of the surfactants are prepared by dissolving appropnate weights in methanol to give concentrations of 1% (1 gm/100 ml). Metal cation solutions are prepared by dissolving their corresponding salts in 0.1 M HCL (or HNO_3) to a final metal concentration of 01.-0.2 M. Anion solutions are prepared in distilled water, dilute acid or alkali solutions. Pesticide solutions are prepared in ethanol, methanol or distilled water.

TLC Plate Preperation or Coating Procedures

The contemporary trend is of using commercially available pre-coated plates. The manual preparation of layers involves the coating of slurry of the adosorbent (silica gel, alumina and soil) on glass, aluminium or plastic sheet (20-20 or 20-10 cm) with the help of TLC applicator. The thickness of dried layer for analytical purposes is kept to 0.2-0.3 mm. A binder (starch, gypsum, dextrin or polyvinyl alcohal) is usually added to the layer material to provide better adhesion, mechanical stability and durability.

Sample Application

Sample application is one of the most important steps in the technology of TLC. Improperly applied samples result in poor chromatograms. Sample can be applied as spot or streak using micropipette, microsyringe, metting point capillaries etc. A number of automatic spotters of varying design are available for sample application. The nanoapplicator (Nanomat) is an example of micrometer controlled syringes which has a dynamic volume range of 50-230 nl. Another applicator (Linomat) allows sample application in narrow bands. The application of sample as streak or band provides more

efficient separations. The sample should be completely dried before placing the plate in the developing chamber. Dilute solutions can be applied to the layer either with sorbent drying between successive applications or after bringing the sample solution to proper concentration.

Development Modes

The process of migration of mobile phase through the sorbent layer to effect separation of the sample substance is called development. Ascending development has been the most commonly used mode of development in TLC. Other development modes such as multiple, stepwise, circular two dimensional and revered-phase partition development have also been used to limited extent. The distance for the migration of mobile phase has been kept to 10-12 cm for conventional TLC. While performing the development one should take care of the angle of the development and saturation of chamber apart from other factors.

1.6 CHROMATOGRAPHIC SYSTEMS

The stationary and mobile phases together comprise the chromatographic system. The optimum conditions for separation in TLC are yielded through mutual harmonization of stationary and mobile phases. Their proper selection decides the degree to which effective separations of components in a mixture can be achieved.

Stationary Phase (Layer Sorbent)

A large number of sorbents are available which can be used in TLC. The various types of sorbent layers presently in use may broadly be classified as follows:

(a) Non-surface Modified Layers or Untreated sorbents : The sorbent phases used in the non-modified form include silica gel G, silica gel H, silica gel LS, acidic and neutral alumina, cellulose, polyacrylonitrile, etc.

Silica gel is the most frequently used layer material. It is slightly acidic in nature. At the surface of silica gel the free valencies of the oxygen are connected either with hydrogen of silanol (Si-OH) groups (Fig 2) or with another silicon atom of siloxane (Si-O-Si) groups. The silanol groups represent adsorptive active surface centers that are capable to interact with solute molecules. The ability of the silanol groups to react chemically with appropriate reagents is used for controlled surface modifications. Hence, silica gel is considered as the most favoured layer material in chromatography.

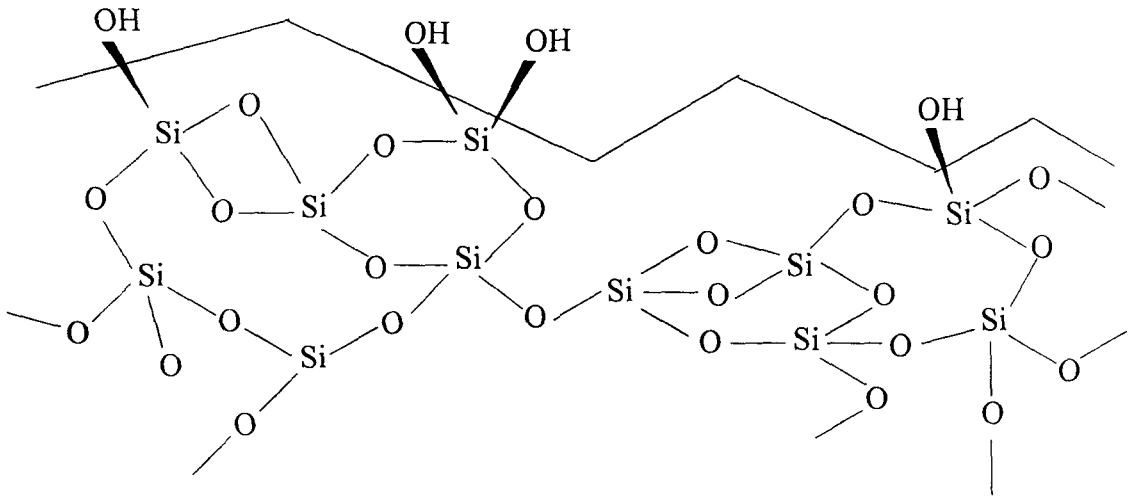

Fig. 2 Structure of Silica gel

(b) Impregnated or Treated Sorbents : To broaden the range of selectivity of above mentioned layer materials in (a), several workers attempted to use these materials after impregnation to a definite degree with buffers, metal ions, chelating agents or high molecular weight organic liquids.

(c) Chemically Modified and Bonded Sorbents: The impregnated layers as mentioned in (b) suffer from the limitations such as

(i) The impregnants are eluted to some extent by the mobile phases used and

(ii) The stripping of liquid stationary phase from the support by incompatible mobile phases.

To overcome these problems, chemically bonded layer materials of similar properties were developed for safer use as stationary phase. Some of the examples are: lipophilic C_{18}-bonded silica gel phases, aminopropyl silica gel (NH_2), octadecyl silica gel (C_{18}) and surface modified cellulose like **ECTEOALA** (a reaction product of epichlorohydrins tri ethanolamine and alkali cellulose).

(d) Inorganic Ion-Exchangers: Apart from silica and alumina, other inorganic ion-exchangers have also found use in TLC. Besides many others, the use of stannic silicate, zirconium phosphoantimonate, zinc ferrocyanide, stannic sulfosalicylate, binder free zirconium (IV) antimonate and hydrous antimony (V) oxide as layer material has also been reported.

(e) Mixed Sorbents: Mixed layers (impregnated and non-impregnated) have been used by several workers for achieving enhanced resolution of components. Mixed layers are usually of medium activity as compared to the separated phases. The addition of kieselguhr or soil in silica generally reduces the activity of silica, resulting in a new sorbent layer with altered activity that is capable of providing peculiar separations, not possible on separated phases.

(f) Miscellaneous Sorbents : These materials include silufol; silufol UV 254; silufol with a layer of silica gel; soil; soil-flyash, soil treated with neutral, alkaline and saline solutions; soil mixed with silica gel and kieselguhr etc.

Mobile phase (Solvent System)

In liquid chromatography including TLC, the mobile phase exerts a decisive influence on the separation. Various optimization schemes (Windows diagram, overlapping resolution maps, simplex method and PRISMA model) have been proposed for normal-phase and reversed-phase TLC. Mobile phase should be as simple as possible and be prepared from the purest grade of the solvent available. Mixtures composed of more than three or four components should be avoided because of problems associated with reproducible preparation. Care must be taken to mix the constituents thoroughly before use. With a particular

sorbent layer, the separation possibility of a complex mixture is greatly improved by the proper selection of mobile phase. The mixture of organic solvents containing some aqueous acid, base or a buffer are, in general, well suited for the separation of ionic species whereas anhydrous organic solvents and water containing mobile phases are more useful for separating non-ionic species. The following mobile phases have been used as developers.

(a) **Organic Solvents :** The single component mobile phase including acetone, acetonitrile, benzene, carbon tetrachloride, chloroform, dioxane, ethanol, ethylacetate, methanol, o-xylene, petroleum ether, toluene, n-octanol, n-nonane, cyclohexane and binary/ternary mixtures of alcohols, amines, ketones, phenols and haloalkanes have been used.

(b) **Inorganic Solvents:** Being non-toxic and non-volatile, solvent systems of this group have been widely used in TLC of inorganics and organometallics. This group includes the solution of mineral acids, alkalis, inorganic salts prepared in double distilled water or water-methanol mixture.

(c) **Mixed Solvents:** Mixtures of two or more different solvents, most of which have either a base (NaOH, NH_4OH and amine) or an acid (mineral or carboxylic) as a component, are used to develop the TLC plate.

(d) **Surfactant-mediated Solvents:** Solutions of surfactants (SDS, CTAB or Triton X-100) have also been used but to a lesser extent as mobile phase in TLC.

The traditional mobile phase systems as mentioned above (a-c) have been widely used in TLC analysis of organic as well as inorganic substances. However, the use of surfactant-mediated mobile phase systems in TLC is of recent origin. These systems, though, have found extensive use in HPTLC, there use in TLC has been limited.

1.7 Visualization

Physical, chemical, enzymatic or biological detection methods are commonly used in TLC. A book by Jork et al. [17] is an excellent source of general information about physical and chemical methods of detection. Physical method of detection involves the use of spectroscopy or autoradiography, X-ray fluorescence microanalysis with a scanning collimated primary X-ray beam, UV radiation etc. Among the physical methods, visualization under UV-light is most common. The chemical detection methods involve the spraying of plates with a suitable reagent, which forms coloured compounds with the separated species. However, reagents giving sufficiently sensitive colour reactions with several species are generally preferred. The biological detection methods (bio-autography) are useful for specific detection of compounds with certain physiological activity.

1.8 QUALITATIVE ANALYSIS

(a) Identification: In TLC, the identification of separated compounds is primarily based on their mobility in a suitable solvent, which is described by the R_F value of each compound, where

$$R_F = \frac{\text{Distance of solute motion from the origin}}{\text{Distance of solvent motion from the origin}}$$

The factors which influence the magnitude of R_F are nature of sorbent and mobile phases, layer thickness, activation temperature, sample volume, chamber saturation, relative humidity and mode of development technique.

(b) Separation: When two or more analytes have differential migration with the same chromatographic system, they are mixed thoroughly the mixture is spotted on the TLC plate and chromatographed. The separated components of mixture are detected and their R_F values are recorded. Some of the basic requirements for a good separation are

(a) Each spot should be compact (R_L-R_T<0.3)

(b) The difference in R_F values of two adjacent spots should be atleast 0.1.

(c) No complexation should occur between/among separable species.

(d) Chromatography of individuals and the mixture should be performed under identical experimental conditions.

1.9 QUANTITATIVE ANALYSIS

The three main approaches related to quantitation TLC include visual estimation and spot size measurement, zone elution and in-situ densitometry.

Visual Estimation and Spot- Size Measurements

This is the simplest method of semi quantitative analysis. TLC plates with a definite sample aliquot along side standards containing known weights of analyte are simultaneously developed. After detection, the weight of analyte in the sample is estimated by visual comparison of the size and intensity of the standards and sample zones.

Zone Elution: In this case, quantitation is performed after scraping off the separated analyte zone, collection of the sorbent and recovery of the substance by elution from the sorbent. Thereafter, the eluates are analyzed by applying any current method of microanalysis, such as electro analytical, Gas Chromatography (GC), spectrophotometery, titrimetry etc.

***In-situ* Method:** *In-situ* densitometry is a preferred technique for quantitative TLC involving the measurement of visible or ultra violet absorbance, fluorescence or fluorescence quenching directly on the layer. The measurements are made either by transmission through the plates, by reflection from the plate, or by reflection and transmission simultaneously using either single beam, double beam or single beam dual wavelength operation of scanning instruments.

1.10 ADVANTAGES OF TLC

TLC is the most versatile and flexible chromatographic method (i) It is rapid because precoated layers are available for use as received, without

preparation (ii) It has highest sample through out because upto 30 individual samples and standards can be applied to a single plate and separated at the same time (iii) The automated sample applications and developers allow high accuracy and precision in quantification (iv) There is a wide choice of layers, developers and detection methods (v) The wide choice of detection reagents leads to unsurpassed specificity. (vi) Less pure samples can be specifically analyzed, as the layers are normally not reused. (vii) Being an "off-line" method, different steps of the procedure are carried out independently. (viii) TLC has distinct advantages over HPLC eg. greater detection possibilities, more rapid throughput, use of disposable plate, easier sample preparation, low solvent consumption and lower operational cost. (ix) Modern TLC can be complementary to HPLC. It allows the processing of many samples in parallel, providing low cost analysis of simple mixtures for which the sample work load is high. (x) The TLC plate act as "storage detectors" of the analyte if they are saved.

1.11 Soil

The term soil is derived form the Latin word 'Solum' which means floor. For a layman or an urban bred, soil is the dirt or debris on the surface of the earth or an inert uniform brown coloured material in which plants find their foot hold. To an agriculturalist soil is a natural medium for plant growth. According to Jenny (1941), soil is a naturally occurring body that has been evolved owing to combined influence of climate and organisms, acting on parent material, as conditioned by relief over a period of time.

According to the glossary of soil (Soil Science Society of America, 1970) "soil" is

(1) The unconsolidated mineral material on the immediate surface of the earth that serves as a natural medium for the growth of land plants.

(2) The unconsolidated mineral matter on the surface of the earth that has been subjected to and influenced by genetic and environmental factors of parent

material, climate (including temperature and moisture effects, macro-and micro-organisms and topography, all acting over a period of time and reducing a product, that is soil, that differs from the material from which it is derived in many physical, chemical, biological and morphological properties and characteristics.

The soil is the key component of terrestrial ecosystem and is essential for the growth of plants as well as for recycling of dead biomass. It is a complex heterogeneous medium consisting of minerals, organic solids and aqueous as well as gaseous components. The minerals presents are usually rock fragments and secondary minerals (phyllosilicates or clay minerals), oxides of Fe, Al and Mn and sometimes carbonates (usually $CaCO_3$). The term 'oxides' include all forms of oxides including hydrous oxides and oxyhydroxides. The organic matter comprises living organisms (mesofauna and micro organisms), dead plant material (litter) and colloidal humus formed by the action of microorganisms on plant litter.

The soil is dynamic system, subject to short-time fluctuations, such as variations in moisture status, pH and redox conditions and also undergoing gradual alternations in response to changes in management and environmental factors. These changes in soil properties affect the form and bioavailability of metals.

Composition of Soil

The four major components of soil are air, water, mineral matter and organic matter. The relative proportions of these four components greatly influence the behaviour and productivity of soil. In a soil, these four components are mixed in a complex pattern; however, the proportion of soil volume occupied by each component can be represented as shown in Fig. 3. The figure shows the approximate proportions (by volume) of the components present in a surface soil in good condition for plant growth. Only about half of the soil

volume consists of soil material (mineral or organic); the other half consists of pore spaces filled with air or water.

The proportion of various soil components may vary from time to time and from place to place. The inorganic (mineral) material is relatively permanent, but the organic material may vary depending upon the location of the site from where the soil sample has been collected. The volume of water and air in soils fluctuate on the basis of particle size, porosity, humidity, temperature of the soil environment etc.

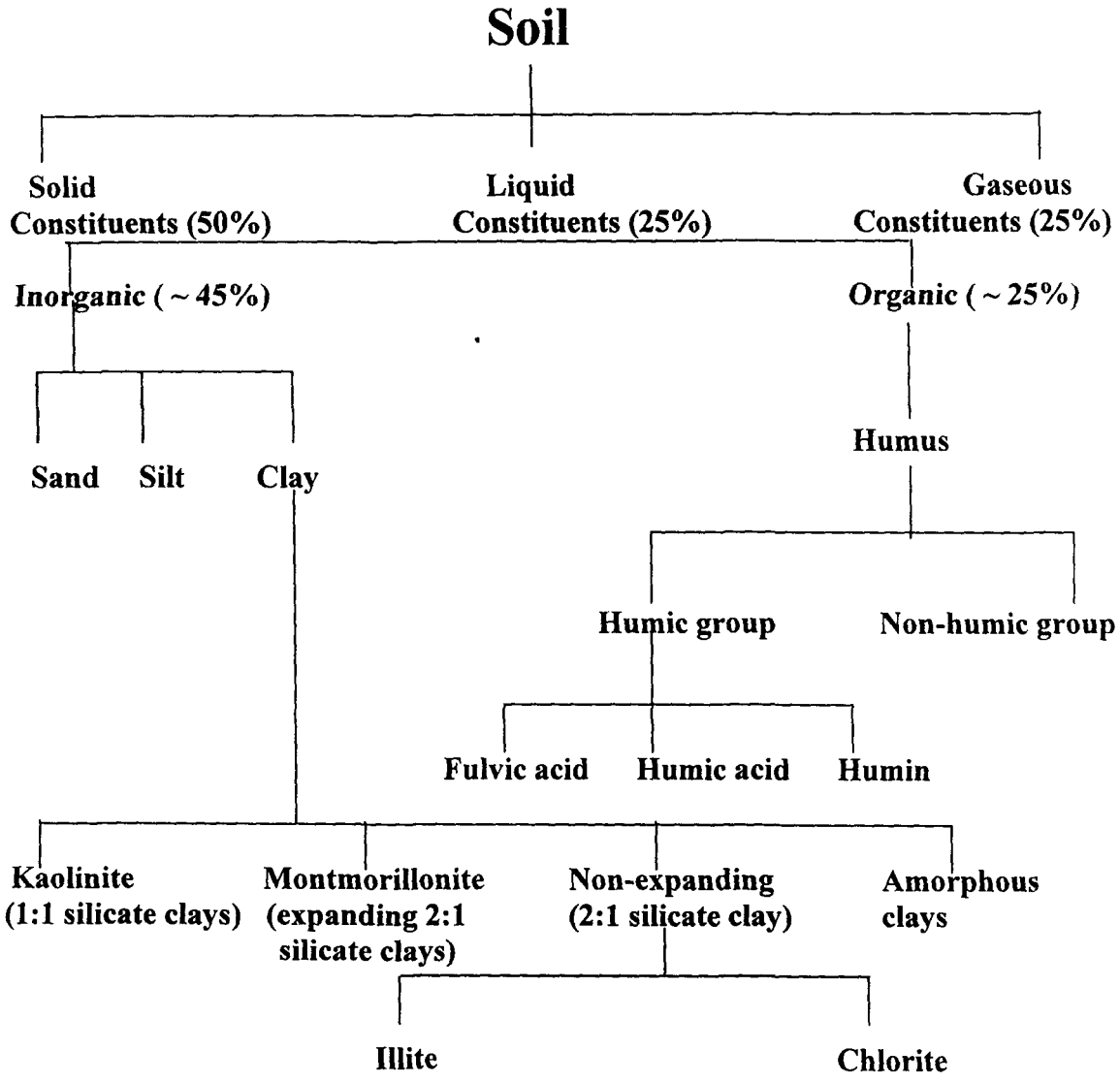

Fig. 3. Approximate Compositions of Surface Soil

Physio-Chemical Properties of Soil

The knowledge of physico-chemical properties of soil is important in understanding soil behaviour. Soil scientists use texture, soil pH, electrical conductivity, colour, cation exchange capacity and other physico-chemical properties of soil horizons in classifying soil profiles and in making determinations about soil suitability for agricultural and environmental projects.

Soil colour

Soil displays a wide range of colour which includes red, brown, yellow, black, dull grey, white or even green. Soil colour varies from place to place in the landscape, as when adjacent soils have different surfaces horizon colours. Colours also typically change with depth through the various layers within a soil profile.

Thee major factors have the greatest influence on the colour of a soil:

(i) its organic matter content

(ii) its water content

(iii)the presence and oxidation states of iron and manganese oxides.

Soil colour has little effect on the behaviour and use of soil. However, it provides valuable clues to the nature of other soil properties and conditions.

Soil texture

The first information required about a soil is its mechanical composition. The mechanical composition or texture means the particle of various sizes such as gravel, sand, silt and clay in soils. Knowledge of the proportion of different sized particles in a soil is necessary for understanding the soil behaviour. Soil texture and structure help determine the ability of the soil to hold and conduct the water and air necessary for sustaining life. The particle

size distribution in soil has its impact on the water holding capacity of soil. It also influences the strength and compressibility of soils. The success of any mechanical analysis primarily depends upon the preparation of sample to ensure complete dispersion of all aggregates into their individual particles without breaking up the particles, and secondarily upon the accurate fractionation of the sample into various fractions.

Soil pH

The soil pH is an approximate measure of an active traction of hydrogen ions present in the soil phase. The pH of the soil applies to the H^+ (ions) concentration in the solution present in soil pores.

The degree of soil acidity or alkalinity, expressed as soil pH , is a master variable that affects a wide range of soil properties - chemical, biological and indirectly, even physical. This chemical variable greatly influences the availability for root uptake of many elements, including both nutrients and toxins.

Among the ways that pH level affects soil physical properties in its influence on the dispersion of clays and the formation and stabilization of aggregate structure. High degree of acidity effectively stabilize large soil aggregates at very high pH levels, the reverse may occur with a dispersed, structureless condition prevailing.

Many complex factors affect soil pH , but none more than two simple balances: the balance between acid and non acid cations on colloid surfaces and the balance between H^+ and OH^- ions in the soil water. These balances, in turn, are largely controlled by the nature of the soil colloids, their charged surfaces, and the compliment of exchangeable cations they attract. Soil pH is also affected by the changes in redox potential which occur in soils that

become water logged periodically. Soil have several mechanisms which serve to buffer pH to varying extents, including hydroxyl, aluminium ions, carbon dioxide, carbonates and cation exchange reactions. However, even with these buffering mechanisms, soil pH differs significantly due to localized variations within the soil.

Electrical Conductivity

Pure water is a poor conductor of electricity, but conductivity increases as more and more salt is dissolved in the water. Thus, the electrical conductivity (EC) of the soil solution gives us an indirect measurement of the salt content. The EC can be measured both on samples of soil or on the bulk soil in situ. It is expressed in terms of decisiemens per meter (ds/m). The salinity is due to the presence of nickel and Na_2SO_4 as soluble salts in soil.

Cation Exchange

Most heavy metals (with certain exceptions, including the metalloids As, Sb and Se and the non-metals Mo and V) exist mainly as cations in soil solution, and their absorption therefore depends on the density of negative charges on the surfaces of the soil colloids. Inorder to maintain electroneutrality, the surface negative charge is balanced by an equal quantity of cations. Ion exchange refers to the exchange between the counter ions balancing the surface charge on the colloids and the ions in the soil solution. It hast the following characteristics: Ion-exchange is reversible, diffusion controlled and stoichiometric process which involves the preference for one ion over another by the adsorbent. The cation exchange capacity (CEC) of mineral soils can range from a few to 60 C mols/Kg but in organic soil it may exceed 200 C mols/Kg.

1.12. Soil TLC

In 1968, Helling and Turner coupled favorable features of TLC and soil and developed a new technique known as "Soil thin-layer Chromatography" and successfully utilized for the monitoring of pesticides movement using different types of soil as static phase. Many other workers had also utilized soil TLC for the investigation of the mobility of various pesticides, trace elements, heavy metal cations and amino acids.

The movement of substances or their separations in TLC can be effected by altering the conditions of the static phase (soil) of diverse nature, developer and applied substances.Thus, soil provides a very fascinating field of research which can be utilized for investigating problems in various applied and non applied fields.

1.13. Literature

The research work performed on TLC analysis of organic and inorganic substances has been well documented in the form of several reviews, monographs, books and articles [23-33]. CRC Handbook of chromatography series in 1972 under the joint editorship of G. Zweig and J. Sherma, and continued since 1991 by the latter and the Handbook of Thin Layer Chromatography published in 1992, 1996 and 2003 under the editorship of B. Fried and J. Sherma have covered nicely the literature of TLC. Further, the latest work carried out on TLC is continiously being reviewed biennially in the Fundamental Reviews of Analytical Chemistry by J. Sherma. The last review of this series has appeared recently [34]. The work published on TLC of pesticides, metal ions and surfactants during the last 15 years has been presented briefly in Tables 1.3, 1.4 and 1.5

Table.1.3 Literature on TLC Studies of Anions and Metal Ions Performed During 1991-2007

Title	Analyte	Remarks/Comments	Ref.
TLC of inorganic ions on p-aminobenzyl cellulose in both sulfuric acid and acid-ammonium sulfate media.	Forty nine inorganic ions	Qualitative separation of inorganic ions on p-amino cellulose with aq. H_2SO_4 (0.01-1.0 M) and H_2SO_4 + ammonium sulfate systems.	1
Chromatography of inorganic ions on diethyl- (2-hydroxypropyl) amino ethyl cellulose layers in hydrochloric acid and in hydrochloric acid-ammonium chloride media.	Inorganic ions	Selective separation of Re (VII) from many inorganic ions on diethyl (2-hydroxypropyl) amino ethyl QE-cellulose with aq. HC1 and HC1 + ammonium chloride systems.	2
Thin layer chromatography of metal ions on a new carbamide-formaldehyde polymer.	Several metal ions	Separation of metal ions of different valency states on cellulose and synthesized carbamide formaldehyde polymer with neutral and acidic solvent systems.	3

1. T. Shimizu, R. Igarashi,Y. Hayashi,and S. Jindo, *J. Planar Chromatogr.–Mod TLC*, 1991, **4,** 487-489.
2. K. Ishida, S. Ninomiya,Y. Uchida and M. Osawa, *J. Chromatogr.*, 1991, **539,** 169-175.
3. N. U. Perisic- Janjic, S. M. Petrovic, and S. Podumavac, *Chromatographia,* 1991, **31,** 281-284.

Title	Analyte	Remarks/Comments	Ref.
TLC of inorganic ions on p-aminobenzyl cellulose developed with hydrochloric acid-ammonium chloride mobile phases.	Forty nine inorganic ions	Qualitative separation of inorganic ions on p-aminobenzyl cellulose with aq. HCl and HCl-ammonium chloride mixtures.	4
Thin layer chromatographic behavior and separation of Zirconium(IV) and hafnium (IV) on silica gel in mineral acid-hydrogen peroxide media.	Zr and Hf	Complete separation of Zr from mixtures containing Zr : Hf ratios ranging from 20:1 to 1:40 on silica gel with HNO_3 + HCl or H_2SO_4 containing different concentrations of hydrogen peroxide.	5
Extraction of lanthanides and some associated elements by mono (2-ethyl hexyl) phosphoric acid and their separations.	Ce^{2+}, Ce^{4+}, Nd, Eu, Gd, Tb, Yb, Y, Ti, V, Zr and Th.	The R_f values of the lanthanide ions increase with increasing concentration of citric acid in mobile phase on silica gel coated with different concentrations of primine JM-T.	6
Ion exchange of alkali metals on zinc ferrocyanide.	Alkali metals	Qualitative separation on zinc ferrocyanide with aq. ammonium nitrate.	7

4. A. Shimizu, S. Jindo and D. Kanoh, *J. Planar Chromatogr. – Mod. TLC*, 1991, **4**, 261-263.
5. K. Ishida, S. Ninomiya, Y. Uchida and M. Osawa, *J. Chromatogr.*, 1991, **539**, 169-175.
6. A. Jain, O. V. Singh and S. N. Tandon, *J. Radional. Nucl. Chem.*, 1991, **147**, 355-361.
7. N. D. Betenekov, G. V. Buklanov, E. G. Ipatova and Yu. S. Korotkin, *RadioKhimiya*, 1991, **33**, 163-168.

Title	Analyte	Remarks/Comments	Ref.
Diatomite as sorbent for thin-layer chromatography of rare elements.	Rare-earth elements	Qualitative separations on diatomite with solutions of acids, bases and salts.	8
Thin-layer chromatography of metal ions on chitin and chitosan bed.	Cu, Co, Cd, Hg, Ni and Ag	Qualitative separations and determination of chromatographic parameters as a function of the concentrations of MeOH, NH_3, and inorganic salts in the mobile phase on chitin and chitosan.	9
Chelation ion chromatography on DMSO impregnated silica gel-G layers: specific separation of cadmium, tungsten, and zirconium from transitional metal ions.	Ni, Cu, Zn, Pd, Cd, Cr, Fe, Rh, La, Au, Tl, Zr, Pt, Nb, Ta, Mn, Ag, Hg, Co, Mo, and W	A correlation between R_F values on silica gel "G", silica gel impregnated layers developed with DMSO-THF (1 + 10) and the atomic numbers of the metal ions exists.	10

8. S. E. Gasparyan, V. A. Sarkezyan and D. S. Gaibakyan, *Arm. Khim Zh.*, 1991, **44,** 417-422.
9. J. K. Rozylo, D. Gwis-Chomicz and I. Malinowska, *Chem. Anal.*, 1991, **36,** 279-287.
10. S. D. Sharma and S. Misra, *J. Liq. Chromatogr.*, 1991, **14,** 3301-3310.

Title	Analyte	Remarks/Comments	Ref.
Chitin, chitosan and their derivatives as stationary phases in thin layers chromatography.	Transitional metal ions	Qualitative study of transition metal on chitin and chitosan with several aq. mobile phases.	11
Separation and identification of cations by TLC.	Twenty-one inorganic cations	Separation and identification of cations using six detection reagents on cellulose with acetylacetone + acetone + concentrated HCl (5 + 5 +1).	12
Chromatographic studies on hydrous oxides of polyvalent metals. Part 1: Thin layer chromatography of anions on hydrous antimony (V) oxide.	Seventeen anions	Qualitative separations of anions on anhydrous antimony (V) oxides with aq. organic acids.	13
Effect of heavy metals on the chromatographic separation of periodate from iodate, borate, iodide, molybdate and ferrocyanide.	IO^{3-}, Io^{4-}, BrO^{3-}, I^-, MoO_4^{2-} and $Fe(CN)_6^{4-}$	Effect of heavy metals on the chromatographic separation of periodate from other oxyanions and cyanoferrates on silica gel layers with distilled water.	14

11. I. Malinowska and J. K. Rozyl, *J. Planar Chromatogr. -Mod. TLC*, 1991, **4,** 138-141.
12. J. Z. Netto, Eclet. Quim. 1991, **16,** 9-13.
13. A. K. Misra and R. P. S. Rajput, *Proc. Natl. Acad. Sci.* India, Sect. A, 1991, **61,** 469-473.
14. A. Mohammad and S. Tiwari, *J. Planar Chromatogr, -Mod. TLC*, 1991, **4,** 485-487.

Title	Analyte	Remarks/Comments	Ref.
Chromatography of anions on alumina thin-layers: Effect of transition metals on Cl^-, Br^-, I^- and NO^{2-}, NO_3^- separations.	Eighteen anions	Investigations of the effect of transition metals on Cl^-, Br^-, I^- and NO^{2-}, NO_3^- separations on alumina, alumina plus silica gel layers with mixed acidic-organic solvents containing formic acid.	15
Chromatography of anionic pollutants on silica gel layers: selective microgram separation of NO^{2-} and IO^{3-}.	Several anions	Microgram detection and separation of anions on silica gel impregnated with aq. salt solutions of Cu, Zn, Ni, Co with acetone mixed with DMSO, formic or mineral acid.	16
Chromatographic separation and quantitative determination of metal ions in wool material.	Fe, Cu and Mn	Qualitative and quantitative studies of metal ions on cellulose with ethanol + isobutanol + conc. HCl + water.	17
Determination of heavy metals by thin-layer chromatography square wave anodic stripping voltammetry.	Pb, Cd and Zn	Determination of heavy metals by TLC-square-wave anodic stripping voltammetry.	18

15. A. Mohammad, M. Ajmal, N. Fatima and J. Ahmad, *J. Liq. Chromatogr.*, 1991, **14**, 3283-3300.
16. A. Mohammad and S. Tiwari, *Microchemical J.*, 1991, **44**, 39-48.
17. Lj. Bokic, M. Petrovic, M. M. Kastelan and K. Moskalinte, *Chromatographia,* 1992, **34,** 648-650.
18. J. H. Aldstadt and H. D. Dewald, *Anal. Chem.* 1992, **64**, 3176-3179.

Title	Analyte	Remarks/Comments	Ref.
Reversed phase TLC behaviour of 3d metal ions in high molecular weight amine-succinic acid systems.	Mn, Co, Ni, Cu, Zn, Fe, Cr, Ti and V	Qualitative identification of 3d metal ions on silica gel coated with high molecular weight amines with aq. succinic acids.	19
Retention of some metal ions on silica gel modified with alizarin red S.	Eleven metals ions	Study of retention behaviour of metal ions from aqueous solutions (pH 1-7) on impregnated layers with a mixture of alizarin red S and aliquot 336.	20
Fluorescence reactions of inorganic cations heated on a porous glass sheet for thin-layer chromatography.	Mg, Al, Ca, V, Cu, Zn, Ge, Y, Zr, Mo, Ag, Cd, In, La, Ce, Eu, Tb, Tl, Pb and Bi	Detection limits and R_F values of fluorescent cations separated on porous glass sheet with n-butanol + benzene + 1M HNO_3 + 1M HCl (75 + 69 + 4 + 2, v/v) or acetone + 3M HCl (99 + 1, v/v)	21
Qualitative analysis for cations within analytical groups by thin-layer chromatography.	Cations	Qualitative separations of cations on cellulose with various solvent systems.	22

19. K. S. Panesar, O. V. Singh and S. N. Tandon, *J. Planar Chromatogr. -Mod. TLC*, 1992, **5**, 289-291.
20. S. Prezeszlakowski and M. Maliszewaka, *Chem. Anal.*, 1992, **37**, 545-550.
21. M. Yoshioka, H. Araki, M. Seki, T. Miyazaki, T. Utsuki, T. Yaginuma and M.Nakano, *J. Chromatogr.*, 1992, **603**, 223-229.
22. Z. Soljic and Z. Hrestak, *Kem. Ind.*, 1992, **41**, 415-420.

Title	Analyte	Remarks/Comments	Ref.
Some observations on the sorption behaviour of heavy metals on layers prepared from mixtures of silica and inorganic ion-exchange gels.	Metal ions	Qualitative separations of metal ions on mixtures of silica and inorganic ion – exchanger gels with sixteen different solvent systems.	23
Sorption recovery of metal ions on silica gel modified with an aza analog of dibenzo-18-crown-6.	Fe, Co, Zn, Cd, Cu and Ni	Application for the analysis of alloys and natural water samples on silica gel modified with analog of dibenzo -18 – crown - 6	24
Normal phase, reversed phase, and chelation thin layer chromatographic studies of some toxic metal ions in two component solvent systems containing DMSO: Quantitative separation of lead from diatomic mercury, mercury, thallium, bismuth, tin, and antimony	Toxic metals	Quantitative separation of Pb from synthetic alloys on plain and silica gel loaded with various concentrations of EDTA or TBP with DMSO – HNO_3 and DMSO – HCI systems.	25

23. A. Mohammad, M. Ajmal, N. Fatima and M. A. M. Khan, *J. Planar Chromatogr. –Mod. TLC,* 1992, **5,** 368-375.
24. E. I. Morosanova, L. S. Selivestrova and Y. A. Zolotov, *Zh. Anal. Khim.*, 1993, **48,** 617-623.
25. S. D. Sharma, S. Misra and R. Gupta, *J. Liq. Chromatogr.*, 1993, **16**, 1833-1843.

Title	Analyte	Remarks/Comments	Ref.
Thin – layer chromatographic determination of inorganic anions as counter – ions of metal – diantipyrylmethane cationic complexes and diatipyrylmethane cations	Cl^-, Br^-, I^-, NO^{2-}, NO_3^-, ClO_3^-, ClO_4^-, $H_2PO_4^-$, SCN^- and SO_4^{2-}	Separation of inorganic anions as diantipyrylmethane using radial or ascending technique on trimethyl hydroxypropylamine cellulose with acetone + chloroform (3 + 1)	26
Identification and separation of some anions on plain and mixed adsorbent layers using water as eluent.	Some anions	Separation of anions in the presence of hardness causing salts. Identification of NO_2^- in artificial sea water on silica gel 'G', alumina, cellulose	27
New surface modified sorbent layers for the analysis of toxic metals in seawater and industrial wastewater.	Toxic metals	TLC analysis of toxic metals present in sea water and industrial wastewater.	28

26. O. Shadrin, V. Zhivopistsev and A. Timberbaev, *Chromatographia,* 1993, **35,** 667-670.
27. A. Mohammad and S. Tiwari, *Microchemical J.*, 1993, **47**, 379-385.
28. A. Mohammad and M. A. M. Khan, *J. Chromatogr.*, 1993, **642,** 455-458.

Title	Analyte	Remarks/Comments	Ref.
Mobility of cadmium as influenced by soil properties, studied by soil thin-layer chromatography.	Cadmium	Examination of mobility of cadmium in various natural soils. The results of soil TLC show the strong control of soil properties on the mobility of cadmium wastes from industrial mining and farming applications.	29
Reversed-phase TLC on inorganic ions on silica impregnated with a high-molecular weight amine using sulfuric acid and sulfuric acid-ammonium sulfate mobile phases.	Forty-nine inorganic ions	R_f values increase with increasing acid or sulfate concentration in the mobile phase, using arseno-silicates of Sn (IV), Cr(III), and Sb(V).	30
Reversed phase TLC and column chromatographic separations of 3d transition metal ions using mono (2-ethyl hexyl)acid phosphate as impregnant.	3d series transition metal ions	Examination of mobility pattern of metal ions as a function of concentration NHO_3 on silufol.	31

29. M. Sanchez Comazana and M. J. Sanchez – Martin, *J. Chromatogr.*, 1993, **643**,357.
30. T. Shimizu, S. Jindo, N. Iwata and Y. Tamura,*J. Planar Chromatogr. –Mod. TLC*, 1994, **7**, 98-102.
31. S. K. Yadav, O. V. Singh and S. N. Tandon, *J. Planar Chromatogr. –Mod. TLC*, 1994, **7**, 75-76.

Title	Analyte	Remarks/Comments	Ref.
Stannic sulfosalicylate: A new adsorbent for quantitative TLC separation of uranium from other important metal ions using mixed dimethylformamide systems.	Uranium	Selective separation of uranium from synthetic mixture of several metal ions on silica gel impregnated with high molecular weight amines with mixtures of DMF and HNO_3 or HCI mobile phase.	32
TLC of inorganic ions on trimethyl hydroxyl propyl amine cellulose eluted with sulfuric acid organic solvent mobile phases.	Inorganic ions	Separation of polyvalent ions and tetravalent rare earths which tend to form anionic sulphate complexes on silica gel impregnated with mono-2-ethyl hexyl acid phosphate with mobile phase sulfuric acid and organic solvents.	33
Thin layer chromatographic detection of copper with 2-thiobarbutric acid.	Copper	TLC of Cu after extraction from biological tissues by dry oxidation on silica gel 'G' with MeOH + acetic acid.	34

32. S. A. Nabi, W. U. Farooqui and N. Rahman, *J. Planar Chromatogr. –Mod. TLC*, 1994, **7**, 38-40.
33. T. Shimizu, S. Jindo, M. Satoh and Y. Mura, *J. Planar Chromatogr. –Mod.TLC*, 1994, **7**, 412-415.
34. D. M. Jogadankar, V. B. Patil and H. N. Katkar, *J. Planar Chromatogr. –Mod. TLC*, 1994, **7**, 166.

Title	Analyte	Remarks/Comments	Ref.
Oxygen flask-TLC micro determination of binary and ternary mixtures of Hg (II), Cu(II) and Cd(II) in their organic compounds and some pharmaceutical preparations.	Hg, Cu and Cd	UV spectroscopic determination of metal ions after elution with H_2O. TLC system was comprised of silica gel 60 and benzene + acetone + DMF (5:4:1).	35
New surface modified sorbent layers for chromatographic analysis of inorganic pollutants.	Inorganic metal cations	Study on migration behaviour of metal cations on surface-modified silica layers with aqueous solutions of formic acid and sodium formate.	36
Chromatography of some cations and anions on mixed sorbent layers in tributyl-phosphate-formic acid system.	Cations with some anions	Quantitative separation of cations and anions on silica gel impregnated with mono-2-ethylhexyl acid phosphate with aqueous MeOH containing tributyl phosphate and formic acid.	37

35. M. E. M. Hassouna, S. M. Sayyah, El-Salam and H. M. Abd, *Anal. Lett.*, 1994, **27**, 2535.
36. A. Mohammd, N. Fatima and M. A. M. Khan, *J. Planar. Chromatog. –Mod. TLC*, 1994, **7**, 142-146.
37. A. Mohammad, M. Ajmal, N. Fatima and R. Yousuf, *J. Planar Chromatogr. –Mod. TLC*, 1994, **7**, 444-449.

Title	Analyte	Remarks/Comments	Ref.
Study of chromatographic behaviour of some inorganic ions on silica gel thin layers.	Inorganic ions	Examination of relationship between concentration of IBMK/FA and the R_F values of ions on silica gel.	38
Effects of amine-pretreatment of silica gel on the TLC behaviour of rare earths.	Rare earths	R_f values of each metal decreased with increasing pK_a value of amine used for pretreatment of silica gel with NH_4CI mobile phase.	39
Reactions of inorganic ions with organic reagents on microcrystalline cellulose and silica gel thin layer. I	Inorganic ions	Study of inorganic ions on microcrystalline cellulose with HCOONa (1.0M) + KI (1.0M) in 1:9 ratio.	40
Application of two phase aqueous systems based on waer-soluble polymers in extraction and thin layer chromatography for recovering and separating actinides.	Actinides	Separation on the basis of different sorption behaviour of actinides in their tetra and penta valency states on silica gel impregnated with polyethylene glycol.	41

38. Y. Jianjan, Gansu Gongye *Daxue Xuebao*, 1995, **21**, 104-108.
39. Y. Takeda, T. Nagai and K. Ishida, Fresenius *J. Anal. Chem.*, 1995, **351**, 186-189.
40. Z. Soljic, Z. Hrestak and I. Eskinja, *Kem. Ind.*, 1995, **44**, 219-234.
41. N. P. Molochnikova, V. M. Shkinev and B. F. Myasoedov, *Radiokhimiya*, 1995, **37**, 517-521.

Title	Analyte	Remarks/Comments	Ref.
Identification, quantitative separation and recovery of copper from spiked water and industrial wastewater by TLC-AAS and TLC-titrimetry.	Cd, Zn, Cu and Pb	Quantitative separation of Cu(II) by AAS after TLC separation from other metals on silica gel with HCOONa (1.0M) + KI (1.0M) in 1:9 ratio.	42
TLC separation of transition metal ions and their quantitative estimation by atomic absorption spectroscopy.	Transition metals	Separation of transition metals with pyridine + benzene + acetic acid + H_2O (6+5+8+4, 5+5+4+1) and BuOH + benzene + formic acid (5+10+9) on silica gel impregnated with EDTA, dimethylglyoxime or 1, 10-phenanthroline.	43
TLC separation and microgram detection of metal ions on lithium chloride-impregnated silica gel and aluminium layers.	Heavy metals	Qualitative separation and detection of heavy metals on silica gel and alumina impregnated with LiC1 with mobile phase HCOOH (1.0M), HCOONa (1.0M) and their mixtures.	44
Separation and identification of metals in human bones, placenta and milk and in air by adsorption and ion-exchange thin-layer chromatography	Heavy metals	Identification of metals in human bones, placenta, milk and air by adsorption and IE-TLC.	45

42. A. Mohammad, *J. Planar Chromatogr. –Mod. TLC*, 1995, **8,** 463-466.
43. V. K. Gupta, I. Ali, U. Khurana and N. Dhagarra, *J. Liq. Chromatogr.*, 1995, **18**, 1671-1681.
44. A. Mohammad and M. A. M. Khan, *J. Planar Chromatogr. –Mod. TLC*, 1995, **8,** 134-140.
45. S. C. Petrovic and H. D. Dewald, *J. Planar Chromatogr. –Mod. TLC*, 1996, **9,** 269-272.

Title	Analyte	Remarks/Comments	Ref.
The determination of some heavy metal cations by TLC/photodensitometrty.	Ni, Co and Cu	Determination of metals in rock samples by TLC/photodensitometry.	46
Studies on the mobility of heavy metals in soil.	Heavy metals	Examination of mobility of some heavy metals Ni, Mn, Cr, Cu and Pb using soil with decomposed organic matter as well as soils amended with commonly used pesticides (thiometon, malathion, dichlorovos, trichloroacetic acid, p-chloro phenoxyacetic acid and β-naphthoxyacetic acid etc.). The mobility of the heavy metals followed the order Ni > Mn > Cr > Cu > Pb in all systems studied.	47
Determination of 17 trace elements in Zr.-U alloys by TBP chromatography and ICP-AES.	Trace elements	ICP-AES determination of Zr in Zr-U alloys after separation by TLC on TBP coated polymeric supports.	48

46. S. Savarci and M. Akcay, *Turk. J. Chem.*, 1996, **20,** 146-152.
47. S. U. Khan, M. A. Qureshi and J. B. Singh, Indian *J. Environmental Health*, 1996, **38**, 1-6.
48. S. Wang and D. Xi, *J. Li. Yejin Fenxi*, 1996, **16**, 12-15

Title	Analyte	Remarks/Comments	Ref.
The separation of some components by TLC on NaX molecular sieves.	Fe and Cr	The separation of Fe^{3+} and Cr^{3+} as well as some anions of elements on molecular sieves NaX	49
On-plate square-wave stripping voltammetry of Cd(II), Cu(II) and Pb(II) at a mercury film ultramicroelectrode after separation by TLC.	Cd, Cu and Pb	Detection limits for Cd and Pb were 1 and 4 μg respectively.	50
Thin-layer chromatography of metal ion on, immobilized chondroitin sulfate plate prepared by plasma polymerization technique.	Co, Fe and Cu	TLC of metal ions on silica gel impregnated with sodium salt of condroitin sulfate with mobile phase consist of aqueous or organic solvents of different pH values.	51
TLC determination of metal cations and nitrogen trichloride in process media.	Metal cations	Determination of Fe in process media by employing 8-hydroxy quinoline as complexing agent.	52

49. P. Evelina, B. Anisoara, P. Angelica, G. Maria and M. Cruceanu, *Chem. Ing. Chim.*, 1996, **42**, 121-124.
50. S. C. Petrovic and H. D. Dewald, *J. Planar Chromatogr. –Mod. TLC*, 1996, **9**, 269-272.
51. K. Yoshimura, T. Horita and K. Hozumi, *Polym. J*, 1996, **28**, 261-265.
52. S. B. Germanov, L. P. Sharova, T. F. Demchuk, N. I. Damoilenko and F. V. Guss, *Khim. –Farm. Zh.*, 1996, **30**, 54-56.

Title	Analyte	Remarks/Comments	Ref.
TLC separation, colorimetric determination and recovery of thiocyanate from photogenic waste, river and sea water.	Several anions and cations.	TLC separation on cellulose microcrystalline, kieselguhr and cellulose plus kieselguhr with NH_4OH (1.0M) + acetone (1:9, 3:7, 1:1; 7:3, 9:1) and colorimetric determination of SCN in water and wastewater.	53
Consecutive thin-layer chromatographic separation of Zr(IV), Hf(IV) and many other ions on silica gel in nitric acid hydrogen peroxide media.	Sixty four ions	Selective separation of Zr(IV), Hf(IV) and many other ions on silica gel with HNO_3 and HNO_3+H_2O_2.	54
Thin-layer chromatographic methods for the identification, estimation and separation of toxic metals in environmental samples.	Toxic metals	Qualitative and selective separation of toxic heavy metals.	55
Possibility of formation of colored spots of inorganic ions with organic reagents on thin layers of cellulose and silica gel II.	Different valencies of several ions	Selective separation and identification of metals of different valency states on microcrystalline cellulose and silica gel.	56

53. A. Mohammad and J. P. S. Chahar, *J. Chromatogr. A.*, 1997, **774**, 373-377.
54. Y. Takeda and K. Ishida. *Talanta,* 1997, **44**, 849-843.
55. A. Mohammad, *J. Planar Chromatogr. -Mod. TLC*, 1997, **10,** 48-54.
56. Z. Soljic, Z. Hrestak and I. Eskinja, *Kem. Ind.* 1997, **46**, 195-202.

Title	Analyte	Remarks/Comments	Ref.
Study and application of thin layer chromatography of metal complexes.	Metal complexes	The study and application of TLC of Co and Ni complexes was detected on thin layers.	57
Chromatographic separation of inorganic ions on thin layers of lanthanum silicate ion exchanger.	Several metal ions	Separation of metal ions on lanthanum silicate ion exchanger with aqueous and mixed solvent systems.	58
Determination of lead and cadmium by stripping voltammetry after separation from humic acid by thin layer chromatography	Pb and Cd	Separation of lead and cadmium from humic acid.	59
Planar chromatography of d-block metal ions on stannic phosfate silicate layers in buffered EDTA solutions: quantitative separation of zirconium from other metal ions.	d-block metals	Binary and ternary separations of d-block metals on stannic phosphate silicate layers with buffered EDTA solutions.	60

57. S. Shaomin, Z. Shengwan, H. X. Guo and L. Lin, *Shanxi Daxue Xuebao, Ziran Kexueban*, 1997, **20**, 405-408.
58. S. W. Husain and A. Mirzai, *Chromatographia.* 1997, **45**, 347-350.
59. S. C. Petrovic and H. D. Dewald, *Anal. Lett.*, 1998, **31**, 2077-2091.
60. S. D. Sharma, S. Misra and A. Agarwal, *J. Indian Chem. Soc.*, 1998, **75**, 410-412.

Title	Analyte	Remarks/Comments	Ref.
Simultaneous identification of mixtures of inorganic cations by two-dimensional thin-layer chromatography.	Twenty inorganic cations	Detection of inorganic cations by two-dimensional TLC on microcrystalline cellulose with two mobile phases, 1-butanol saturated with 1:1 mixture of 3M HNO_3 and (a) 1 M HCl (b) MeOH + 36% HCl (10+3, v/v)	61
Analysis of metal chlorosuplhates on layers prepared from chicken egg-shell powder and its mixtures with cellulose or silica.	Metal chlorosulfates	Examination of mobility and selective separation of metal chlorosulfates with acid containing mobile phases and aqueous ammonium sulfate solution (1.0M).	62
A theoretical study of the thin-layer chromatographic behaviour of 33 metal ions on silica gel.	Thirty three metal ions	The study of retention sequence of metal ions on silica layers with methyl isobutyl ketone and formic acid.	63
Analytical capabilities of micellar mobile phase in the thin layer chromatography of metal 1,3-diketonates.	1,3-Diketones of heavy metals	The study of 1-3 diketones and other metal ions on silufol and plasmachrom plate with micellar mobile phases containing sodium dodecyl sulfate.	64

61. T. Yoshinaga, T. Miyazaki and H. Akel, *J. Planar Chromatogr. –Mod. TLC*, 1998, **11**, 295-299.
62. A. Mohammad, K. T. Nasim and M. P. A. Najar, *J. Planar Chromatogr. -Mod. TLC*, 1998, **11**, 127-131.
63. H. Zhang, Y. Gengliang, Y. Jianjun, Z. Hongyi and S. Hanwen, *J. Planar Chromatogr. -Mod. TLC*, 1998, **11**, 51-55.
64. S. N. Shtykov and E. G. Sumina, *J. Anal. Chem.*, 1998, **53**, 446-450.

Title	Analyte	Remarks/Comments	Ref.
TLC of facial and meridional isomers of Co(III) and Cr(III) complexes on polyacrylonitrile sorbent.	Co and Cr complexes	Some qualitative separations were achieved on polyacrylonitile.	65
Micellar thin-layer chromatographic separation of heavy metal cations: Effect of organic and inorganic additives on migration behaviour.	Heavy metal cations	Selective separation of heavy metal cations by micellar TLC on microcrystalline cellulose.	66
Chromato-spectrophotometric determination of cobalt with preliminary separation from nickel on tributyl phosfate impregnated layers prepared from silica gel and stannic arsenate gel mixture.	Co and Ni	Mutual separation of Co^{2+} and Ni^{2+} on mixed stannic arsenate gel and silica gel 'G' in (10:1, w/w) layer impregnated with 0.2M tributyl phosfate with 1.0M aqueous potassium thiocyanate containing mobile phase.	67
Detection, identification and separation of certain heavy metals on silica gel-supported stannic arsenosilicate layers.	Thirteen metal ions	Detection and separation of heavy metals on silica gel mixed with Sn(IV) arsenosilicate and impregnated with tributylamine with methanol containing mobile phase.	68

65. Z. L. Tesic, T. J. Sobo, S. R. Trifunovic and D. M. Milokovicopsenica, *J. Chromatogr. A.*, 1999, **847**, 297-301.
66. A. Mohammad, E. Iraqi and I. A. Khan, *J. Surfactants and Detergents*, 1999, **2**, 523-529.
67. A. Mohammad, M. P. A. Najar and E. Iraqi, *Indian J. Chem. Technol.*, 1999, **6**, 38-42.
68. A. Mohammad, S. Anwar and E. Iraqi, *Chem. Anal.*, 1999, **44**, 195-200.

Title	Analyte	Remarks/Comments	Ref.
Colorimetric determination of silver in synthetically prepared ores with preliminary separation from associated metal ions by thin-layer chromatography.	Several metal ions including Ag	Selective separation of Ag^{+} from other metal ions on microcrystalline cellulose, alumina 'G' and their binary mixtures with ammonia, acetic acid and sodium or ammonium salt solutions containing mobile phase.	69
Separation of some inorganic species by thin layer chromatography; Part (II) separation Cu^{2+}, Co^{2+}, Ni^{2+} Cd^{2+} and UO_2^{2+} ions by thin layer chromatography on silica gel 'G'	UO_2^{2+}, Cu^{2+}, Ni^{2+} and Cd^{2+}	TLC study of metal ions on silica gel 'G' with mixture of acetone, water and acetic acid or HC1.	70
Influence of some chemical fertilizers on the mobility of trace metals through soil amended with flysah.	Trace metals	Investigation of effect of some organic compounds on the mobility of trace metlas viz; Co, Zn, Cu, Ag and Pb through soil amended with flyash. The results indicate decrease in the mobility of trace metals with increasing dosage of flyash in soil but with a variation in intensity by the use of organic compound as mobile phase (eg. acetaldehyde, acetone, formaldehyde, ethyl methyl ketone etc.).	71

69. A. Mohammad and J. P. S. Chahar, *J. AOAC. Int.*, 1999, **82**, 172-176.
70. S. L. Sharifi and S. S. Dhaktode, *Orient. J. Chem.*, 2000, **16**, 79-84.
71. S. U. Khan, J. A. Khan, R. K. Bhardwaj and S. Jabin, *J. Indian Chem. Soc.*, 2000, **77**, 326.

Title	Analyte	Remarks/Comments	Ref.
Quantitative determination of Mg in Al-alloys by ion-exchange TLC.	Mg and Al	Ion-exchange TLC separation of Mg and Al on amberlite IRP-69 and microcrystalline cellulose mixed in different ratio with 0.5-2.0 M HCl and HNO_3.	72
New adsorbents in planar chromatography: II. Behaviour of metal ions on titanium (IV) silicate ion-exchanger.	Thirty metal ions	TLC separation of metal ions on titanium (IV) silicate ion-exchanger with aqueous and mixed mobile phases.	73
Applicability of surfactant-modified mobile phases in thin layer chromatography of transition metal cations:identification and separation of zinc(II), cadmium(II), and mercury in their mixtures.	Metal ions	Identification and separation of Zn^{2+}, Cd^{2+} and Hg^{2+} using surfactant containing mobile phase systems on silica gel 'G'.	74

72. Y. Duan, Fujian Fenxi Ceshi, 2000, **9**, 1182-1187.
73. V. Ghoulipour and S. W. Husain, *J. Planar Chromatogr. –Mod. TLC*, 2000, **13**, 354-358.
74. A. Mohmmad, E. Iraqi and I. A. Khan, *Chromatogrphy*, 2000, **21**, 29-36.

Title	Analyte	Remarks/Comments	Ref.
Quaternary separation of some transition metal chlorosulphates on mixed adsorbent layer with water as mobile phase: Quantitative determination of nickel chlorosulfate.	Chlorosulfates of Mn, Fe, Co, Ni, Cu and Zn	Separation of nickel chlorosulfate from manganese, iron, copper or zinc chlorosulfate on silica gel-cellulose (2:1, w/w) with double-distilled water.	75
A new visualization reagent for cation separation by TLC.	Several metal ions	Qualitative separation of a mixture of cations and their identification with 0.01% 9-formylacridine solution in dichloromethane on cellulose 'R'.	76
TLC of some cations and their separation by naturally occurring mixed oxides impregnated plates.	Metal ions	Separation of metal ions from their binary mixtures using TLC plates impregnated by mixed oxides.	77
Retention behaviour of some d and f block metal ions on untreated and tri-n-butylamine-impregnated silica gel G layers-quantitative separation of Zr^{4+} and W^{6+} from other metal ions and alloy components.	D and f block metal ions	TLC study of Zr^{4+} and W^{6+} with BuOH-8M HNO_3 and aqueous HNO_3.	78

75. A. Mohammad and V. Agrawal, *J. Planar Chromatogr. –Mod. TLC*, 2000, **13,** 210-216.
76. A. Patrut, C. Marutoiu, O. F. Marutoiu and M. I. Moise, *J. Planar Chromatogr. –Mod. TLC*, 2000, **13,** 151-153.
77. R. K. Ghatuary, A. K. Mukhopadhyay and C. K. Sarkar, *J. Indian Chem. Soc.*, 2000, **77**, 106-107.
78. S. D. Sharma and C. Sharma, *J. Planar Chromatogr. –Mod. TLC*, 2000, **13,** 93-100.

Title	Analyte	Remarks/Comments	Ref.
Micellar mobile phases for the TLC separation of some transition metal ions and their 1, 3-diketonates.	1, 3-diketonates of metal ions	TLC separation of metal ions and their 1, 3-diketonates on silufol and RP-plazma chrom with 2.5 x 10^{-2}M aqueous SDS.	79
A new chromatographic-iodometric method for the separation and determination of iodide and its oxyanions.	I^-, IO_3^- and IO_4^-	Separation and determination of iodide and its oxyanions on aluminium oxide 'G' with mixtures of NH_4OH and CH_3COCH_3 different ratio.	80
Sorption behavior of certain metal ions in normal phase and reversed phase TLC using layers of silica zirconium tungstophosfate gels.	Fourteen heavy metal ions	Sorption behavior of metal ions in normal phase and reversed phase TLC using plain, mixed and TBA impregnated silica gel 'G' layers with various aqueous and alcoholic organic solvents.	81
Qualitative thin layer chromatographic identification and separation of some metal peptidoglycan monomer complexes on cellulose.	Metal peptidoglycan monomer complexes.	Quantitative TLC, identification and separation of some metals and their peptidoglycan monomer complexes on cellulose.	82

79. S. N. Shtykov, E. G. Sumina and N. V. Tyurina, *J. Planar Chromatogr. –Mod. TLC*, 2000, **13,** 266-270.
80. A. Mohammad, J. P. S. Chahar, E. Iraqi and V. Agrawal, *J. Planar Chromatogr. –Mod. TLC*, 2000, **13**, 12-15.
81. A. Mohammad and E. Iraqi, Indian *J. Chem. Tech.*, 2000, **7**, 223-226.
82. L. Sesartic, O. Hadzija and N. Brajenovic, *J. Liq. Chromatogr. Relat. Technol.*, 2001, **24**, 1511-1514

Title	Analyte	Remarks/Comments	Ref.
Thin layer chromatography of inorganic ions on blended inorganic ion exchangers with tributyl phosphate-formic acid mobile phase.	Inorganic ions	TLC separation of IO_3^- from NO_2^- and BrO_3^- on stannic arsenate or tin (IV) molybdosilicate plus silica gel, alumina or cellulose (1:9) with tri-n-butylphosphate-water-formic acid system.	83
Thin layer chromatographic separation of anions by naturally occurring mixed oxides impregnated plates.	Anions	Separation of anions on TLC plates coated with naturally occurring clay mineral.	84
Quaternary separation of some transition metal chlorosulphates on mixed adsorbent layer with water as mobile phase: Quantitative determination of nickel chlorosulfate.	Chlorosulfates of Mn, Fe, Co, Ni, Cu and Zn	Separation of nickel chlorosulfate from manganese, iron, copper or zinc chlorosulfate on silica gel-cellulose (2:1, w/w) with double-distilled water.	85
Thin layer chromatographic separation and recovery of gold and silver from secondary sources.	Several metal ions	TLC coupled with spectrophotometry and titrimetry for quantitative separation of Au^{3+} and Ag^+ from accompany ing metal ions on silica gel 'G' and alumina 'G' with aqueous CTAB (1.2mM) and aqueous $(NH_4)_2SO_4$ (2.5M).	86

.83. A. Mohammad, R. Yousuf and Y. Hamid, *Acta Chromatographica*, 2001, **11,** 171-182.
84. R. K. Ghatuary, A. K. Mukhopadhyay and C. K. Sarkar, *J. Indian Chem. Soc.*, 2001, **78**, 492-494.
85. A. Mohammad and M. P. A. Najar, *Acta Chromatogrpahica*, 2001, **11**, 154-170.
86. A. Mohammad, S, Syed, L. M. Sharma and A. A. Syed, *Acta Chromatographica*, 2001, **11**, 183-195.

Title	Analyte	Remarks/Comments	Ref.
Separation of nickel (II) and copper (II) from different cations by TLC using dipentyl dithiophosphoric acid as complexing reagent.	Ni and Cu	TLC separation of Ni and Cu with mobile phase o-xylene-methyl ketone (MEK)-N, N-DMF (16:2:1, v/v) mixed with dipentyldithiophosphoric acid.	87
Use of non-ionic poly (ethyleneglycol) p-iso octyl-phenyl ether (Triton X-100) surfactant mobile phases in the thin layer chromatography of heavy metal cations.	Heavy metal cations	TX-100 was used as a mobile phase in the TLC separation of heavy metal ions on silica gel layers	88
Thin layer micellar chromatography of coinage metal cations.	Metal cations	Thin layer chromatography of metal cations using surfactant-mediated mobile phase on conventional TLC plates.	89
Application of TLC-MALDI-TOFMS to identification of Co(II) and Co(III) acetylacetonates.	Acetylacetonates of Co(II) and Co(III)	The compounds were detected by their mass spectra, comparative study of analytes with TLC and conventional MALDI-TOFMS.	90

87. M. L. Soran, C. Marutoiu, M. Curtuc, T. Hodisan and R. Oprean, *Acta Universitatis Cinbiniensis. Seria F: Chemia*, 2002, **5**, 69-73.
88. A. Mohammad, E. Iraqi and I. A. Khan, *Chromatographic Sci.*, 2002, **40**, 1-8.
89. A. Mohammad and Y. H. Sirwal, *J. Planar Chromatogr. –Mod. TLC*, 2002, **15**, 107-115.
90. K. Matsumoto, H. Ajiro, S. Habane and Y. Okamoto, *J. Mass Spectrometry Soc. Japan*, 2002, **50**, 15-17.

Title	Analyte	Remarks/Comments	Ref.
Thin layer chromatography of anions-separation of coexisting hexacyanoferrate (II), hexacyanoferrate (III) and thiocyanate with a new mobile phase.	Eighteen anions	TLC of eighteen anions was performed on silica layers with mixed aqueous organic mobile phases.	91
Retention behaviour of inorganic anions as mixed silica gel G-starch layers: Quantitative separation of F^-, MoO_4^{2-}, AsO^{3-}_4 and $Cr_2O_7^{2-}$ from other anions.	Twenty five anions	The retention behaviour of 25 anions on 1:1 silica gel G-starch layers was studied using two component non aqueous mobile phase or aqueous solution of organic acids and their Na salts.	92
TLC studies and separation of heavy metal cations on soil amended silica gel layers developed with surfactant-mediated solvent systems.	Metal cations	Identification of best TLC system for metal cations separation from their multicomponent mixtures on soil mixed with silica layers. N-Cetyl-N, N, N-trimethyl ammonium bromide (CTAB) with edit urea was found to be the most favourable mobile phase.	93
New TLC system for simultaneous separation of iron, cobalt and nickel ions from acidic and ammonical solutions.	Metal cations	Separation of metal cations with novel TLC system. Proposed method is useful for specific separation of iron (III), cobalt (II) and nickel (II).	94

91. A. Mohammad and V. Agrawal, *J. Planar Chromatogr. –Mod. TLC*, 2002, **14**, 371-377.
92. S. D. Sharma and C. Sharma, *Indian J. Planar Chromatogr. –Mod. TLC*, 2003, **16**, 237-243.
93. A. Mohammad and N. Jabeen, Indian *J. Chem. Technol.*, 2003, **10**, 79.
94. A. Mohammad, E. Iraqi and Y. H. Sirwal, *Sepn. Sci. Technol.*, 2003, **38**, 2255-2278.

Title	Analyte	Remarks/Comments	Ref.
Novel solvent system for the separation of Cr (VI) from Cr (III) and associated heavy metal cations by high performance thin-layer chromatography.	Eleven heavy metal cations	Heavy metal cations were chromatographed on silica gel HPTLC plates with pure organic, mixed organic and mixed aqueous- organic mobile phases.	95
Separation studies of transition metal ions with cationic micellar eluents in normal phase thin-layer chromatography.	Metal cations	TLC separation and identification of metal cations was studied on silica gel plates with hybrid mobile phase.	96
Thin-layer chromatography of certain metal cations with anionic micellar mobile phase systems: Simultaneous separation of co-existing gold (III), copper (II), silver (I) and spectrophotometric measurement of Cu (II) from associated metal cations on silica layer developed with anionic micellar mobile phases.	Metal cations	TLC of metal cations on silica gel layers with surfactant- mediated mobile phase. Quantitative determination of Cu (II) was done by spectrophotometer.	97

95. A. Mohammad and Y. H. Sirwal, *Acta Chromatogrphica*, 2003, **13**, 117-134.
96. A. Mohammad, V. Agrawal and N. Jabeen, *Chromatography*, 2003, **24**, 135-145.
97. A. Mohammad, Y. H. Sirwal and S. Hena, *Chromatography*, 2003, **24**, 135-145.

Title	Analyte	Remarks/Comments	Ref.
Chromatographic behaviour of metal ions on egg shell layers.	Metal cations	The TLC of metal ions were performed in twelve solvent system on egg shell layers.	98
Separation of some cations by TLC using dibutyl dithio-phosphoric acid as complexing reagent.	Metal cations	Separation of some cations on silica gel 'H' and Zr (IV) silicate plates using a mixture of o-xylene-methyl ethyl ketone (MEK)- N-N DMF (16:2:1; v/v) as mobile phase.	99
Adsorption studies of metal cations on silica static flat-bed using anionic micellar mobile phase systems containing carboxylic acids: Separation of co-existing iron (III), copper (II) and nickel (II).	Several metal ions	TLC of metal ions on silica gel 'G' layers with surfactant- mediated mobile phase. Spectrophotometric determination of Fe (III).	100

98. A. K. Misra, *Indian J. Chem. Technol.*, 2003, **10**, 367-369.
99. M. L. Soran, C. Marutoui, M. Curtui and M. Dascalu, *Chem. And Environ. Res.*, 2003, **12,** 135-139.
100. A. Mohammad, V. Agrawal and S. Hena, *Adsorption Sci. and Technol.*, 2004, **22**, 89-105.

Title	Analyte	Remarks/Comments	Ref.
Inducement of a new micellar mobile phase for thin-layer separation and quantitative estimation of aluminium (III) in bauxite with preliminary separation from iron (III) and lutetium (IV).	Heavy metal ions	TLC studies of heavy metal cations on silica gel 'G' layers with surfactant-mediated (0.001 M AOT + 1M formic acid; 1:1; v/v) mobile phase. Quantitative estimation of Al^{3+} was also done with spectrophotometer.	101
High performance thin layer chromatography of heavy metal cations with formic acid containing mobile phases: Effect of added organic solvents and surfactants on the mobility of cations.	Heavy metal cations	HPTLC of heavy metal with surfactant-mediated mobile phase containing formic acid.	102
Calibration based estimation of detection and determination limits of Cu (II) and Ni (II) for a TLC analytical system.	Cu (II) and Ni (II)	Detection and quantification limits were calculated for extraction. TLC of Cu (II) and Ni (II) ions with dialkyl dithio phosphoric acids in a polar solvent system.	103

101. A. Mohammad and S. Hena, *Sepn. Sci. and Technol.*, 2004, **39**, 2731-2750.
102. A. Mohammad and Y. H. Sirwal, *Indian Chem. Technol.*, 2004, **11**, 726-731.
103. C. Sarbu, L. Soran and M. Curtui, *Revista de chimie.*, 2004, **55**, 137-139

Title	Analyte	Remarks/Comments	Ref.
Separation of ionic rhodium and iridium species by electophoresis on reversed phase thin-layer chromatography plates.	Metal ions	RP-TLC was effectively used for the separation of metal ions in low concentrations by classical low-voltage electrophoresis. Electrograms of rhodium (III) and iridium (IV) were obtained.	104
Use of Micellar Anionic Surfactant Solutions with Added Carbohydrates as Mobile Phase in Thin-Layer Chromatography of Heavy Metals Cations- Separation of Mixtures of Aluminium (III), Manganese (II) and Chromium (VI).	Metal ions	Separation of aluminium (III), manganese (II) and chromium (VI) using micellar surfactant with sugars on silica gel.	105

.104. A. P. Gumenyuk, S. P. Mushtakova, D. M. Vadeneev and L. F. Kozhina, *J. Anal. Chem.*, 2004, **59**, 146-149.
105. A. Mohammad and H. Shahab, *Acta Chromatographica*, 2005, **15**, 192-205.

Table 1.4 Literature on TLC studies of surfactants performed during 1991-2006.

Title	Analyte	Remarks/Comments	Ref.
Effect of nature of support and impregnating agent on a lipophilicity for non-ionic surfactants by reverse phase thin-layer chromatography.	Nonionic surfactants.	The retention of 9 nonyl phenyl ethoxylate oligomers was determined in 15 reverse phase chromatographic systems using silicone oil of various molecular weight as impregnating agents and silica, cellulose and alumina supports. The retention value did not follow the additivity rule and they did not change linearly with increasing length of the ethylene oxide chain probably due to the folded state of the chain in the eluent. Retention increasing with increasing level of impregnation.	1
The identification of anionic detergents by thin layer chromatography.	Anionic surfactants	Surfactants are identified by TLC on silica gel plates using BuOH-HoAC-iso PrOH (3:1:0.5) solvent systems and azure and dragendroff reagent for visualization under UV light. Detection limit 2 μg.	2
The identification of anionic detergents by thin layer chromatography.	Anionic surfactants	Anionic surfactants were identified by TLC on silica gel plates using BuOH-HOAc-iso PrOH (3.1:0.3) solvent system and azure A and dragendorff reagent for their visualization.	3
Separation of fatty components by solid phase adsorption. Part II. Determination of fatty substrates in fat liquoring baths other applications.	-	The method was used for analysis of fat liquoring baths from natural and synthetic fats.	4

1. T. Cserhati and Z. Illes, *Chromatographia.*, 1991, **31**, 152-156.
2. S. Akinci and K.C. Guven, *Acta Pharm. Turc.*, 1992, **34**, 121-126.
3. S. Akinci and G. Kasim C, *Acta Pharm. Turc.*, 1992, **34,** 121-126.
4. J. Cot, M. Fort and J. Cartiel, *AQEIC Bol Tec.*, 1992,**43**, 147-157, 162-167.

Title	Analyte	Remarks/Comments	Ref.
Identification of narrow distribution lauryl alcohol ethoxylate by TLC.	Lauryl alcohol ethoxylates	The composition of polyethylene glycol lauryl ether nonionic surfactant was analised by TLC in EtOH solution on silica gel plate using 55:35:10 EtOH-acetone-water mixtures.	5
Characterization of CPC on HPTLC plates by microsurface enhanced Raman Seattering.	Cationic surfactant	The technique was used for in situ study of the adsorption behaviour of CPC on silica gel. SERS is a powerful technique monitoring the behaviour of CS for assessing adsorbate orientation and conformation for proling the effect of various environmental factors and interaction between the adsorbate silica gel-Ag colloid substrate.	6
Solvent strength and selectivity in TLC separation of ethylene oxide oligomers.	Nonionic tenside	Seoeration of various nonionic tenside consisting of ethylene oxide oligomer mixtures. Solvent strength and selectivity were calculated. Selectivity is higher on alumina than on silica gel.	7
Lipophiticity determination of non homologues series of nonionic surfactants by TLC.	Nonionic surfactants	The lipophilicity and specific hydrophobic surface area of 22 nonionic surfactants, having different hydrophobic moieties have been detected.	8
Separation of different types of surfactants by thin layer chromatography.	Surfactants	TLC separation of different types of surfactants has been achieved by multiple development on silica plates.	9

5. Wu. Zhining and Riyong Huaxue, *Gongye*., 1992, **3,** 14-154.
6. E. Koglin, *J. Planar Chromatog*., *–Mod. TLC*, 1993, **6,** 88-92.
7. T. Cserhati, *J. Chromatogr. Sci.,* 1993, **31,** 220-224.
8. J. Cserhati, J. Biochem, Biophysics Methods, 1993, **27,** 133-142.
9. A. Kruse, N. Buschmann and N. Cammann, *J. Planar. Chromatogr*., *–Mod. TLC*, 1994, **7,** 22-24.

Title	Analyte	Remarks/Comments	Ref.
Chromatography of cationic surfactants: HPLC, TLC and GC.	Cationic surfactants	A review with 89 references on analysis of cationic surfactants with HPLC, TLC and GC.	10
Analytical methods for carbohydrate surfactants.	Carbohydrate surfactants	This paper describes two analytical methods for a fast, simple and reliable analysis of alkyl polygluco-sides.	11
Analytical methods for carbohydrate surfactants.	Carbohydrate surfactants	This paper describes two analytical methods for a fast, simple and reliable analysis of alkyl polygluco-sides.	12
Relationship between hydrophile lopophile balance and behaviour in reversed phase thin layer chromatography of some nonionic surfactants.	Nonionic surfactants	An equation was derived to establish the HLB values of polyethoxylated nonionic surfactants (Brij and Triton X series) from TLC parameters.	13
Characterization of polyethylene glycerol trifoliate, a nonionic surfactant by TLC.	Polyethylene glycerol trifoliate	A sensitive, specific and reproducible TLC method was developed for separation of the oligomers of Tagat TO, a polyoxyethylene glycerol trioleate nonionic surfactant.	14
Alkyl polyglycosides (APG) analysis of raw material determination in products and environmental matrixes.	Alkyl polyglycosides (APG)	HTGC, HPLC and TLC are oresebted for the characterization of APG raw material for surfactants in products and environmental matrixes.	15

10. P. B. Mepherson and R. Henvik T, *Surfactant Science Series* 1994, **53,** 289-326.
11. N. Buschmann and S. Woderczark, *Comun. Jorn. Con. Esp. Deterg.* 1994, **25,** 203-207.
12. S. Wardarczak and N. Bushmann, *GIT Frachg Lab.* 1995, **39,** 410-412.
13. C. Attomare, G. Trapani, M. Franco, A. Latrofa and G. Liso, *Acta Technol. Legis Med.*, 1995, **6,** 33-41.
14. M. Rischer, I. Bher, E. Wolf-Henss and J. Engel, *J. Planar. Chromatogr. -Mod. TLC*, 1995, **8,** 382-387.
15. H. Waldoff, J. Scherler and M. Schmitt, *World Surfactants Congr.*, 4th 1996, **1**, 507-518.

Title	Analyte	Remarks/Comments	Ref.
Separation and characterization of surfactants by high performance thin-layer chromatography.	Surfactants	The separation and characterization of dirrerent types of surfactants of all four types has been achieved by HPTLC by single development on silica plates.	16
Thin layer chromatographic behaviour of substrate and products from the synthesis of Gemini type surface active agents.	Gemini type surface active agents	TLC behaviour of substrate and products from the synthesis of Gemini type surface active agents. Silica gel G and acetone benzene were used as stationary and mobile phases. Chromic acid, a mixture of cobalt (II) nitrate and potassium thiocyanate were used for detection.	17
Alkyl polyglycosides (APG) analysis of raw materials; determination in products and environmental samples.	Alkyl polyglycosides (APG)	Analytical methods were developed for APG characterization and detection in products and environmental samples are presented.	18
Use of thin layer and high performance liquid chromatography for the study of the adsorption of surfactants on a river sedimensts.	Surfactants	The adsorption of tri butyl phenolethylenoxide containing various lengths of ethylene phenol on revering sediment was studied by TLC and HPLC.	19
Some chromatographic determination of surfactants in cleaning surfaces.	Surfactants	Separation of surfactant is done by TLC and quantified by SFC according to degree of ethoxylation and alkyl chain length. Retention time determined with HPLC.	20

16. S. Simuric and Z. Soljic, *J. Liq. Chromatogr., Relat. Technol.*, 1996, **19**, 1139-1149.
17. I. Baranowska, E. Zielinski, E. Lekawaska and B. Kozielska, *J. Planar Chromatogr. –Mod. TLC,* 1996, **9**, 189-191.
18. H. Waldhoff, J. Scherler and M. Schmitt, *World Surfactants congr.*, 4th 1996, **1**, 507-518.
19. T. Cserhati, V. Nemeth-Kiss and E. Forgacs, *J. Biochem.* Biophysics Methods, 1996, **33,** 81-88.
20. J. Bohnen, B. Foellner, G. Rohm and H. Kruessmann, *SOFW J.*, 1998, **124, 714,** 716-719.

Title	Analyte	Remarks/Comments	Ref.
Methods of detecting and/or reducing systematic errors in quantitative planar chromatography. Part 2. Systematic errors caused by separation system.	Surfactants	Methods of detecting and/or reducing systematic errors in quantitative planar chromatography. Part 2. systematic errors caused by separation system.	21
Use of a glutamic acid containing aqueous-organic mobile phase for on-plate separation, detection and identification of cationic and non-ionic surfactants by thin-layer chromatography.	Cationic and non-ionic surfactants	A new TLC system comprising silica gel G as stationary phase and a three component mobile phase, 0.1M glutamic acid- methanol-acetone, 1:1:1 (vol./vol.) for separation and identification of cationic and non-ionic surfactants, tetradecyl trimethyl ammonium bromide (TTAB) has been successfully separated from Triton X-100 (TX-100). TLC spectrophotometry was used for quantitative estimation of TTAB.	22
Identification and quantitative determination of priority non-ionic and amphoteric surfactants in raw materials and detergent compositions by high-performance liquid chromatography, thin-layer chromatography and UV spectrometry.	Nonionic and amphoteric surfactants	Procedure for group and individual identification of 5 priority nonionic surfactants and 1 amphoteric surfactant in raw materials and finished detergents with the use of UV spectrometry, TLC, HPLC with diode array and referactometric detectors, and solid phase extraction on ion exchange sorbent. Use of three components acetonitrite methanol-water mobile phase improved the selectivity of the separation of surfactants un comparison with binary acetonitrile-water and methanol-water mixtures.	23

21. E. R. Kaiser, *J. Planar Chromatogr. –Mod. TLC*, 2005, **18,** 118-126.
22. A. Mohammad and H. Shahab, *Acta Chromatographica*, 2006, **17,** 272-291.
23. A. Lobachev and A. Kolotvin, *J. Anal. Chem.*, 2006, **61**, 622-629.

Table 1.5 Literature on TLC studies of pesticides performed during 1991-2007.

Title	Analyte	Remarks/Comments	Ref.
Determination of pesticides in water by HPTLC using automated multiple development (AMD).	Pesticides	Reliable identification of trace amounts of pesticides in ground water, surface water and drinking water.	1
Adsorptive and reversed phase retention characteristics of some modified silica sorbents.	2-nitrro-4-cyano-phenyl esters and triphenyl methane derivatives	The retention characteristics of two pyrolysed and two chemically modified silicas were investigated in adsorptive and reversed phase TLC. The effect of various surface modifications in the case of different homologous series of solutes was studied. The sorbents retain their retention characteristics even after impregnation.	2
Computer assisted comprehensive optimization of mobile phase selectivity in HPTLC.	Org. nitrogen pesticides	The system includes 3 methods: (1) optimum graphics system, (2) multifactor optimization system and (3) computer simulation-diagram optimization. Excellent agreement is obtained between predicted and experimental chromatograms.	3
Use of pesticides in leather industry. Part 1. Determination	Pesticides	Characterization of pesticides using TLC on activated silica gel with benzene-EtOAc (9:1) as solvent, and visualization with fluorescein under UV light. Confirmation can be obtained by reverse phase TLC on K18 with MeOH-H_2O-HOAc (64:33:3) as solvent and visualization with AgNO3 (methylene bisthiolyanate and TCMTB), eosin Y (carbamates) or 4-amino-antipyrine (phenols).	4

1. U. De la Vigne and D. Jaenchen. *J. Planar Chromatogr., –Mod. TLC*, 1990, **3**, 6-9.
2. Z. Illes and T. Cserhati. *J. Planar Chromatogr., –Mod. TLC*, 1990, **3**, 163-8.
3. Q.S. Wang and H. Y. Wang. *J. Planar Chromatogr., –Mod. TLC*, 1990, **3**, 15-19.
4. M. Tomaselli; A. Cozzolino and C. Liccardi, Cuoio, Pelli, Mater. Cocianti, 1990, **66,** 129-54.

Title	Analyte	Remarks/Comments	Ref.
Quantitative determination of organophosphorus pesticides by HPTLC with detection by enzyme inhibition.	Organophosphorus pesticides	Determination of organophosphorus pesticides by HPTLC using inhibition of esterase- 1 produced by *Bacillus subtilis*, 1-thionaphthyl acetate or esterase substrate and 2, 2′-azo (1-naphthol, 8-chloro-3,6-disulfonic acid) 4, 4′ diphenyl disulfide as indicator of SHgps. Ascending TLC was performed with the following elements: 3:1 or 9:1 or 4:1 hexane-acetone; 6:6:3:4 benzene-acetone. Lowest-limit of detection was 0.01 ng; range of detection was 0.1-5 ng.	5
Pesticides	Pesticides	A review with 180 refs. On chromatographic methods of detecting and determining pesticide residues in food and feed; thin layer methods are emphasized.	6
Pesticide analysis in biological samples. Organophosphorus pesticides.	Organophosphorus pesticides	A review with 13 refs. Topics include stability, metabolism, and identification of organophosphorus pesticides in biological samples by thin layer chromatography and mass spectroscopy.	7
Promising analytical technique-direct combination of HPLC and TLC.	Nonionic emulsifiers and pesticides	The HPLC-TLC combined technique is described. A schematic diagram for the system is presented. Three sample separation are described, involving non ionic emulsifiers and pesticides.	8

5. O. V. Vashkevich and E. S. Gankiva, *J. Planar Chromatogr., –Mod. TLC*, 1990, **3**, 354-6.
6. K. Fodor-Csorba, *Chromatogr, Sci.*, 1991, **55**, 663-715.
7. N. Tsunoda, *Jpn. J. Toxicol.* 1990, **3**, 403-7.
8. D. E. Janchen, Lab. 2000 *[Duemila]* 1998, **2**, 32-5.

Title	Analyte	Remarks/Comments	Ref.
Application of AMD to the determination of crop protection agents in drinking water. Part 1: Fundamentals and method.	Pesticides	The fundamentals of the Automated Multiple Development (AMD) technique are discussed. Multiple and stepwise development combined with gradient elution is highly suitable for the systematic detection and determination of pesticides. The analysis is computer controlled. At least 100 substances can be checked for their presence on one TLC plate, and the technique uses only a few milliliters of mobile phase.	9
Application of hydrophilic modified silica gels in TLC.	Vitamins, pesticides, natural substances, DNP amino acids, gallic acid (and esters), preservatives, steroids and progesterones	Amino-,cyano-, diol-modified silica gels are described and their applications as TLC stationary phases are illustrated.	10
Thin-layer chromatography of pesticides.	Pesticides	A review with 115 refs.	11
Identification and quantitation of currently important pesticides by HPTLC.	Pesticides (predominantly fungicides and insecticides)	Determination of over 100 pesticides in standard solution by HPTLC employing modern spotting and evaluation techniques. 3 detection systems used were : cholinesterase inhibition, $AgNO_3$-UV irradiation; and Cl-O-tolidine.	12

9. K. Burger, J. Koehler and H. Jork, *J. Planar Chromatogr., –Mod. TLC*, 1990, **3,** 504-10
10. H. E. Hauck and W. Jost, *Am. Lab. (Fairfield Conn.),* 1990, **20,** 42, 44-5, 47-8.
11. J. Sherma, *J. Planar Chromatogr. –Mod. TLC*, 1991, **4,** 7-14.
12. C. Gardyan and H. P. Their, Z. Lebensm. *Unters. Forsch.,* 1991, **192,** 40-5.

Title	Analyte	Remarks/Comments	Ref.
Application of modern thin layer chromatographic techniques for conformation of results in multi residue analysis.	Pesticides.	HPTLC on silica gel 60 and RP-18-W layers to confirm GLC results in pesticide multi-residue analysis. It was highly efficient and low cost. HPTLC together with the clean up procedure is suitable for multi residue detection and determination.	13
Multiple-development high performance thin layer chromatography of organochlorine pesticides.	Methoxychlor, dieldrin, λ-endosulfan, lindane; P, P -DDD, P, P-DDT, P, P'-DDE and aldrin	Detection of organochlorine pesticides using silica gel 60 precoated plates. The mobile phases were n-heptane-CH_2Cl_2 at variable proportions.	14
Separation and determination of pesticides in samples of environmental importance. Part 1.	Methyl parathion, malathion, sumithion and methomyl	Spectrophotometric determination and separation by TLC. Methyl parathion was determined spectrophometrically as Ni, Cu, Fe, or Co complex at 342, 270, 354 and 345 nm resp., with detection limits of 13, 4.3, 1.07 and 1.1 ppb; resp. The mobile phase used was EtOAc-$CHCl_3$ (1:9).	15

13. C. Gardyan and H. P. Thier Fresenius, *J. Anal. Chem.* 1991, **339,** 338-9.
14. G. Lodi, A. Betti, Y. D. Kahie and A. M. Mohamed, *J. Chromatogr.*, 1991, **545,** 214-18.
15. M. R. Jan, R. Masoud and J. Shah, *J. Chem. Soc. Pak.* 1990, **12,** 337-40.

Title	Analyte	Remarks/Comments	Ref.
Application of high performance thin layer chromatography and automated multiple development for identification and determination of pesticides in water.	Pesticides	Combination of HPTLC with AMD provides both a separation efficiency better than comentional TLC, and reproducible gradient elution on the thin layer. Demonstration of reliable identification of trace amounts of pesticides (eg. 28 ppt of atrazine) in subsoil, surface and drinking water by AMD-HPTLC using a polarity gradient based on dichloromethane.	16
Some aspects and examples of automated multiple development (AMD) gradient optimization.	Phenolic compounds and organochlorine pesticides	Optimization of AMD gradients for HPTLC and presented. Universal gradients optimized for the separation of phenolic compounds spanning a wide polarity range on diol layers; gradient with a low polarity range optimized for the separation of organochlorine pesticides on silica gel layers.	17
Identification and determination of organophosphorus and organochlorine pesticide residues in tomatoes.	Organo phosphorus pesticides (OPP) and organochlorine pesticides (OCP)	The detection threshold for Actellic, Basudin, DDBP, dilor, carbophos, kethane, TXM-3, phosalone, phosphamid, chlorophos, and Hostaquile is determined by GC ranged 0.0002-0.03 mg/kg and determined by TLC ranged 0.01 mg/kg.	18

16. U. De la Vinge, D. E. Jaenchen and W. H. Weber, *J. Chromatogr.*, 1991, **553,** 489-96.
17. G. Lodi, A. Betti, E. Menziani, V. Brandolini and B. Tosi, *J. Planar Chromatogr., -Mod. TLC*, 1991, **4,** 106-10.
18. M. A. Klisenko and M. V. Pismennaya, *Agrokhimiya*, 1990, **6**, 98-103.

Title	Analyte	Remarks/Comments	Ref.
Analytical field screening of soil by thin layer chromatography.	Semi volatile organic compounds including petroleum distillates, polynuclear aromatic hydrocarbons, chlorinated pesticides, polychlorinated biphenyls, phenols and explosives.	TLC as screening tool for on-site environmental level analysis. The technique is qualitative and quantitative in soil and water for a variety of semivolaile organic compounds. Low ppm detection limits can be achieved.	19
Method development for monitoring pesticides in environmental waters: liquid-soilid extraction followed by liquid chromatography.	Pesticides	A method based on liq-solid extn. of pesticides from drinking water followed by HPLC was modified to make it suitable for monitoring pesticides in ground water and river water. Except for two pesticides, the limits of quantification (5 times the limit of detection) for the pesticide in municipal water and ground water samples were 0.1 μg/L.	20
Direct analysis of thin-layer chromatography spots by thermal extraction-gas chromatography mass spectroscopy.	Naphthalene compounds (polycyclic aromatic hydrocarbons and pesticides)	A method of direct analysis of separated or over lapped silica gel TLC spots with naphthalene compounds-PAHs and pesticides. Analytes are identified at the level of 20 ng/spot, and a detection limit is of several hundred picograms. This method can be applied to thermally stable substances that can be desorbed from TLC silica gel.	21

19. J. S. Newborn and J. S. Preston, *Hazard. Mater. Control* 1991, **4,** 56-9.
20. A. Dicorcia and M. Marchetti, *Environ. Sci. Technol.*, 1992, **26,** 66-74.
21. X. Chen and R. B. Smart, *J. Chromatogr. Sci.* 1992, **30,** 192-6.

Title	Analyte	Remarks/Comments	Ref.
Thin-layer chromatography of pesticides.	Pesticides	A TLC method using arsenic trichloride/sulfuric acid as a spray reagent for the detection of pesticides. The sensitivity of the technique was 0.5-2 μg.	22
HPTLC for the confirmation of results in pesticide multiresidue analysis.	Pesticides (predominantly fungicides and insecticides)	The suitability of HPTLC as a confirmator procedure in gas chromatog. (GC) determination of pesticide residue in fruit and vegetables. Optimal determination conditions for 121 pesticides are given; route determination limits were generally 0.01-0.05 mg/kg.	23
An optimized screening system for 170 pesticides.	Pesticides	A review with 13 refs. of the authors own work on the development of a screening program for the systematic forensic and toxicol. Analysis of pesticides based on then TLC detection in combination with GC and UV spectroscopy as independent techniques.	24
Liquid-liquid extraction separation and chromatographic determination of some organochlorine and organophosphorus pesticides in three phase systems.	Organochlorine pesticides (OCP) and organophosphorus pesticides (OPP)	Systems comprised of 36-44% aq K_2CO_3, meOh and diethyl acetamide or DMF for the development of thin layer chromatograms in the anal. of water for 16 OCP and OPP.	25

22. K. K. Chahal, S. K. Grewal and J. C. Kohli, *Natl. Acad. Sci, Lett (India)*, 1991, **14,** 469-70.
23. C. Gardyan, H. P. Thier and Z. Lebensm, *Unters. Forsch.*, 1992, **194,** 344-50
24. F. Erdmann, H. Schnetz, C. Brose and G. Rochholz, Beitr. *Gerichtl. Med.*, 1991, **49,** 121-6.
25. V. A. Frankovskii, V. I. Kofanov and Yu. V. Lushnikova, *Zh. Anal. Khim.* 1992, **47,** 1058-65

Title	Analyte	Remarks/Comments	Ref.
Applications of AMD to the determination of crop-protection agents in drinking water. Part II : Limitations.	Pesticides	Use of thin (100μm) adsorbent layer increases the sensitivity of UV detection by a factor of 2-3; it has no effect in the visible region of the spectrum ; nor on fluorescence measurements. The detection limit is dependent on the response of the substance and on the sample matrix; the prevent limit for triazines is ~50ng/zone.	26
Comparison of HPTLC and HPLC procedures for the determination of certain xenobiotic residues in apples and pears.	Residues of benomyl, carbendazim, ethoxyquin and thiabendazole.	The method showed good precision with a percentage coeff of variation of less than 5%; recoveries were always greater than 90%. Comparision with HPLC confimed the validity of the results.	27
Quantitative high pressure TLC in toxicology.	Opiates, 1, 4 benzodiazepines via aminobenzophenones, phenothiazines, doping agents, barbiturates derivatives and pesticides	A review with 13 refs. HPTLC is a very highly valuable tool for qualitative and quantitative analysis of many compounds which are frequently encountered in toxicological analysis.	28

26. H. Jork, G. Keller and U. Kocher, *J. Planar Chromatogr., -Mod. TLC,* 1992, **5**, 246-50.
27. P. Corti, E. Dreassi, N. Politi and C. Aprea, *Food Addit. Contam.*, 1992, **9**, 243-51.
28. H. Schuetz and F. Erdmann, *GIT Fachz., Lab.* 1993, **37**, 18, 20-2.

Title	Analyte	Remarks/Comments	Ref.
A TLC detection program for 178 pesticides.	Pesticides	The colour reactions of 178 pesticides with 6TLC detection reagents are listed forming a rapid screening system for the detection and identification in forensic and other analysis.	29
Thin layer chromatographic methods for use in pesticide residue analysis.	Pesticides	A review with 290 refs. on stationary phases, mobile phases, detectors and TLC techniques used to detect, separate, determine and identify pesticide residues in various environmental samples.	30
Thin layer chromatographic behaviour of carbamate pesticides and related compounds.	Carbamate pesticides and related compounds	The thin-layer chromatographic behaviour of carbaryl. carbendezim (Bavistin), carbofuran, propoxur, phenol, 4-chlorophenol, o-nitrophenol λ-naphthol and calcium phosphate, calcium sulphate, cellulose and silica gel G in solvents such as acetone, benzene, carbon tetrachloride, chloroform, ethanol and distilled water.	31
The advantage of new bio-imaging analyzer for investigation of the metabolism of ^{14}C-radiolabeled pesticides.	^{14}C-radiolabeled pesticides	The linearity, sensitivity and resolution of new bio-imaging analyzer TLC plate scanner and the results compared with those obtained using a linear analyzer or conventional x-ray autoradiography. The instrument had a wide linear dynamic range the sensitivity was significantly higher and the resolution was far better than that of either the linear analyzer or autoradiography.	32

29. C. Brose, G. Rochholz, F. Erdmann and H. Schvetz, *Beitr. Gerichtl. Med.*1992, **50**, 221-8.
30. H. S Rathore and T. Begum, *J. Chromatogr.*, 1993, **643,** 271-90.
31. H. S. Rathore and T. Begum, *J. Chromatogr.*, 1993, **643,** 321-9.
32. O. Klein and T. Clark, *J. Planar Chromatogr., –Mod. TLC*, 1993, **6,** 368-71.

Title	Analyte	Remarks/Comments	Ref.
High performance thin layer chromatography of several pesticides and their major environmental by-products.	Pesticides	A HPTLC method to separate and detect atrazine, carbofuran, chlorpyrifos, metachlor and some environmental by products in experiments involving bioreactors designed to degrade waste pesticide material. All separation were 1-dimensional and consisted of dual solvent system. The F_{254} indicator prooved to be the best detection method for atrazine, carbofuran, metachlor, and their byproducts. Chloropyrifos was better detected by 1-pyrene carboxaldehyde.	33
Polyethylene polyamines as reagents for thin layer chromatography.	Pesticides	Pesticide detection on Silufol plates; visualization by 10% triethylene tetramine or polyethylenes in acetone. The threshold of detection of metaphos, phosphamide, and Basudin was 0.2 μg/sample, vs. 0.2-0.25 μg/ sample for the tetraethylene pentaamine std.	34
Rapid screening method for pesticides as the cause substances of toxicosis by TLC.	Pesticides	Common pesticides having many toxicities were analysed by fluorescent silica gel TLC with 4 developing solvent systems and 3 detection methods. Method is useful in identification of pesticides as the cause substances of toxicosis rapidly from the serum and returned gastric lavage solution from patients.	35

33. D. N. Judge, E. Mullins and R. W. Young, *J. Planar Chromatogr., –Mod. TLC*, 1993, **6**, 300-6.
34. A. A. Kasatkina, L. P. Ivanova, V. N. Trifonova and G. K. Galeeva, *Zh. Prikl. Khim. (S. Peterburg)* 1993, **66**, 1177-8
35. H. Mori, T. Sato, H. Nagase, Y. Sakai, S. Yamaguchi, Y. Iwata, R. Hashimoto, F. Yamazaki and M. Hayata, *J. Toxicol. Environ. Health,* 1994, **40,** 101-10.

Title	Analyte	Remarks/Comments	Ref.
Evaluation of the mobility of C^{14}-labeled pesticides in soils by thin layer chromatography using a linear analyzer.	C^{14}-labeled pesticides	The mobility of pesticides in a chromic cambisol soil by soil TLC. Pesticide mobilities were determined by autoradiographs and linear analyzer and found to decrease in the following order: acephate > fluometuron > atrazine > ethofumesate > metachlor > diazinon > glyphosate.	36
Reversed-phase thin-layer chromatography of various pesticides in the presence of water soluble beta-cyclodextrin polymer (SCDP).	Pesticides	The modification of hydrophobicity of pesticides with SCDP in presence of aq. NaCl RP-TLC. Pesticides form inclusion complexes with SCDP which are less lipophilic than the parent pesticides. The correlation between lipophilicity and salting out effect increases with increasing polarity (lower lipophilicity) of the pesticides whereas the lipophilicity has negligible effect on the inclusion forming capacity of non homologous series of pesticides.	37
2-Trichloromethyl benzimidazole, a new selective chromogenic reagent for detection of some heteroaromatic pesticides on thin layer chromatographic plates.	Heteroaromatic pesticides	Detection is done with an acetone solution of 2-trichloromethyl benzimidazole. The detection limit is 20 ng to 10 µg depending upon the detected compound.	38

36. M. J. Sanchez-Martin, T. Crisanto, M. Arienzo and M. Sanchez-Camazano, *J. Environ. Sci. Health, Part B* 1994, **B29**, 473-84.
37. Y. Darwish, T. Cserhati and E. Forgacs, *Chromatographia.*, 1994, **38,** 509-13.
38. L. Konopski, *Pestic. Sci.*, 1994, **41,** 335-38.

Title	Analyte	Remarks/Comments	Ref.
Determination of pesticides by thin layer chromatography.	Pesticides	A review with 138 refs. of advances in application of TLC and HPTLC for the separation, detection and qualitative and quantitative determination of pesticides and related compounds. The use of radio-TLC for pesticide metabolism, uptake and degradation studies is also reviewed.	39
Screening of 265 pesticides in water by Thin Layer Chromatography with Automated Multiple Development.	Pesticides	A universal gradient based on dichloro methane was used to check the presence of pesticides from different classes. The data for migration distances, the UV-spectra and the instrumental detection limits were computed.	40
Mobility of pesticides in soils. Influence of soil properties and pesticide structure.	Pesticides	Determination of pesticide mobility using soil TLC and ^{14}C-labeled compounds. According to the R_F values, pesticide mobility varied in the following order: acephate > fluometuron > atrazine > ethofumesate > glyphosate.	41
Relationship between the high performance liquid and thin layer chromatographic retention of non homologous series of pesticides on an alumina support.	Pesticides	Determination of the retentions of pesticides on an alumina HPLC column and in TLC carried out on alumina layers using n-hexane-dioxane mixtures as eluents. The hydrophilic retention parameters on alumina supports have a negligible effect on the type of their biological activity.	42

39. J. Sherma, *J. Planar Chromatogr., –Mod. TLC*, 1994, **7**, 265-72.
40. S. Butz and H-J. Stan, *Anal. Chem.* 1995, **67**, 620-30.
41. T. Crisanato, M. J. Sanchez-Martin, M. Sanchez-Camazano and M. Arienzo, Toxicol. *Enviorn. Chem.* 1994, **45**, 97-104
42. T. Cserhati and E. Forgacs, *J. Chromatogr., A* 1994, **668**, 495-500.

Title	Analyte	Remarks/Comments	Ref.
Use of multiresidue gas chromatographic analysis to determine pesticide mobility on soil TLC plates.	Pesticides	A microextn. technique combined with GC/NPD in order to establish relative mobility of seven co-applied pesticides in soil TLC plates. The mobility of any one pesticide was not affected by the presence of the other co-applied chemicals.	43
Use of correlations between retention parameters in thin-layer and high performance liquid chromatography for the identification of analyte compounds.	Toxic organic compounds (pesticides polymeric material components and products of their decomposition and metabolism)	The retention of analytes belonging to various classes of toxic organic compounds in both normal and reversed phase thin layer and column liquid chromatography. Correlations between the retention parameters of members of homologous series in TLC and HPLC are related to the additivity of the CH_2 group contribution.	44
Computer assisted optimization of pesticides separation by two dimensional high performance thin layer chromatography.	Pesticides	Computer assisted method for optimization of two mobile phase selection for separation of a mixture of pesticides in 2D-TLC. Optimization of separation is based on two polynomial estimation from preliminary runs of two groups. Excellent agreement is obtained between predicted and experimental results.	45
Movement of pesticides in soil thin layer chromatographic systems.	Pesticides	R_f values of pesticides were calculated. Studies showed that attention should be paid to the ground water pollution problem caused by Aldicarb.	46

43. M. Mojasevic and C. S. Helling, *J. Environ. Sci. Health, Part B*, 1995, **B30**, 163-73.
44. V. D. Chmil, L. P. Noritskaya and M. N. Gertsyuk, *Zh. Fiz. Khim.* 1994, **68,** 1763-9.
45. Q. S. Wang, B. W. Yan and L. Zhang, *Chromatographia*, 1995, **40**, 463-6.
46. F. An, H. Mo, K. Yang, X. Yang and Y. Liu, *Huanjing Hanxue* 1995, **14,** 25-31.

Title	Analyte	Remarks/Comments	Ref.
Thin layer chromatography as a pilot technique for HPLC demonstrated with pesticide samples.	Pesticides	Investigation of the transferability of chromatographic conditions from TLC precoated plates to HPLC columns. Different stationary phase (silica gel, RP-18, RP-8, Diol, NH_2, CN) with standard substances and real samples are used. The influence of the matrix is negligible and excellent transfer results are realized.	47
Thin layer chromatography with automated multiple development (AMD-TLC).	Pesticides	AMD is a TLC technique, which combines the wide range of polarity gradient elution on silica with a separation power similar to HPLC. Twelve samples of ground or drinking water can be analysed simultaneously for some dozens of pesticides within one run.	48
Multi method applying AMD-TLC analysis to drinking water.	Pesticides	The technique of AMD-TLC applied to pesticides amenable to TLC with subsequent detection by means of their reflectance spectra recorded with a TLC scanner. A software program enabling easy pesticide recognition by means of a dedicated data base is described.	49
Solid phase extraction for the confirmation of results in polar pesticides residue analysis by HPTLC.	Polar pesticides	HPTLC is a convenient method for confirming the presence and identification of pesticide residues. Tertbutyl Me ether/methanol (99+1) mixture was used as an eluent.	50

47. S. Reuke and H. E. Hauck, Fresenius, *J. Anal. Chem.*, 1995, **35,** 739-44.
48. K. Burger, *Chem. Plant Prot.*, 1995 (Pub. 1995), **12,** 181-95.
49. H. J. Stan and S. Butrz, *Chem. Plant Prot.*, 1995. (Pub. 1995), **12**, 197-216.
50. S. Mouratidis and H. S. Their, Z. Lebensm, –*Unters. Forsch.*, 1995, **201**, 327-30.

Title	Analyte	Remarks/Comments	Ref.
Application of AMD to the determination of crop protection agents in drinking water. Part 5. Fundamentals of a confirmatory test.	Pesticides	Method for the determination of active ingredients of plant protecting products in ground, raw and drinking water. Pesticide extract is fractionated on silica coated TLC plates in screening gradient by AMD. Detection is performed by UV multi detection. The recoveries for pesticides were 80.1 ± 13%.	51
Screening of pesticide contaminated soil by super critical fluid extraction (SFE) and high performance thin layer chromatography with automated multiple development.	Pesticides	Extraction is carried out by supercrit.carbon dioxide (CO_2) with methanol as modifier. Different components of the extracts are separated by HPTLC/AMD and evaluated densitometrically. A 35-step development of the TLC plate with gradient elution offers an application over a wide range of polarity. Migration data, recoveries and detection limits were determined.	52
Computer assisted optimization of two step development high-performance TLC.	Pesticides	Computer assisted method for the optimization of two mobile phase compounds and the selection of development distance of a mixture of 9 components (6 pesticides and 3 unknown compounds) in two step development HPTLC. Excellent agreement between predicated and experimental results is obtained.	53
Computer aided identification of TLC separated pesticides.	Pesticides	Enhancing the reliability and the speed of identification of pesticides by a newly created data base. Solvent systems used are : n hexane-acetone (80:20); toluol-acetone (95:5); chloroform-acetone (50:50). Thin new system is user friendly and interactive.	54

51. K. Burger; H. Jork and J. Koehler, *Acta Hydrochim. Hydrobiol.*, 1996, **24,** 6-15.
52. R. Kober and R. Niessner, Fresenius *J. Anal. Chem.*, 1996, **354**, 464-9.
53. Q. S. Wang, B. W. Yan and L. Zhang, *J. Chromatogr., Sci.* 1996, **34**, 202-5.
54. I. Ionou, D. Kapitanova and K. Blajev, Adv. Forensic Sci., Proc. Meet. Int. *Assoc. Forensic Sci.* 13th, 1995, **5,** 114-117.

Title	Analyte	Remarks/Comments	Ref.
Thin layer chromatographic detection of phosphorathionate and phosphorothiolothionate pesticides using 4-amino-N, N-diethylaniline.	Pesticides	TLC method using a novel chromogenic reagent to detect phosphorothionate and phosphorothiolothionate groups of pesticides.The method is rapid and highly sensitive. The limit of detection is 0.05-05 μg.	55
Pesticide residue analysis in plant food products by TLC with automated multiple development (AMD).	Pesticides	Analysis of insecticides of the thermolabile benzoyl urea group from a fraction of the clean up multi method S19 by AMD-TLC. Detection of benzoyl ureas was facilitated by their exhibiting a maxima at 260 nm.	56
Comparative study of some chromatographic response function (CRF) used in LC and TLC optimization. A new weighted multiple CRF useful for TLC.	Pesticides	A new weighted CRF containing first and second degree terms and its application for the optimization of a ternary solvent system: benzene-petroleum ether-chloroform mixture used for the separation of pesticides.	57
Study of the effect of exogenous organic mater on the mobility of pesticides in soils using soil thin-layer chromatography.	Pesticides	The effect of soil amendment using urban compost, agricultural organic amendments and surfactants on the mobility of two sparingly soluble pesticides-diazinon and linuron. Soil mobility depends upon the organic carbon content of amended soils as well as the amendment nature.	58

55. A. Pasha, Y. N. Vijayshankar and N. G. K. Karanth, *J. AOAC Int.* 1996, **79,** 1009-1011.
56. H. J. Stan and U. Wippo, *GIT Fachz. Lab.* 1996, **40**, 855-858.
57. I. H. Nascu, T. Hodisan and C. Cimpoiu, *Stud. Univ. Babes-Bolyai, Chem.* 1994, **39**, 167-177.
58. M. Sanchez-Camazano, M. J. Sanchez-Martin, E. Poveda and E. Iglesias-Jimenez, *J. Chromatogr. A*, 1996, **754,** 279-284.

Title	Analyte	Remarks/Comments	Ref.
Application of instrumental thin layer chromatography and solid phase extraction to the analysis of pesticides residues in grossly contaminated samples of soil.	Pesticides	Modern TLC equipment for the determination of pesticides residues in soil that was contaminated by petroleum derivatives. Recovery and error of the method were estimated.	59
Thin layer chromatographic behaviour of carbamate pesticides and related compounds on zirconium phosphate layers.	Carbamate pesticides	A new TLC approach based on the use of zirconium phosphate as stationary phase. Rapid identification was carried out using various solvent systems. Carbofuran was strongly retained on the ZrP layers, while the other related compounds showed none or a weaker retention effect. Novel separations were achieved.	60
Determination of pesticides by thin-layer chromatography.	Pesticides	Advances in the application of TLC and HPTLC for the separation detection and qualitative and quantitative determination of pesticides, other agrochemicals and related compounds are reviewed for the period of 1994-1996. Collection of representative chromatographic systems for practical separation and analysis of variety of pesticides.	61

59. J. Bladek, A. Rostkowski and M. Miszczak, *J. Chromatogr., A*,1996, **754,** 273-278.
60. S. Z. Qureshi, R. M. A. Q. Jamhour and N. Rahman, *Chem. Anal.* (Warsaw), 1997, **42,** 41-48.
61. J. Sherma, *J. Planar Chromatogr. –Mod. TLC*, 1997, **10,** 80-89.

Title	Analyte	Remarks/Comments	Ref.
Automated Multiple Development (AMD). Application and on-line coupling with reversed phase HPLC. Part 1. Principles and applications of AMD. Multiple methods for ultratrace determination : plant-protection agents in ground-water and drinking water anlaysed by thin layer chromatography with AMD.	Pesticides	Ground water and drinking water analysis for pesticides using RP-HPLC with on line coupling to AMD TLC. The system is described as a microbore HPLC application with a reversed phase separating column and a modified automatic sampler. Column eluate is sprayed on the silica gel TLC plates. Some results are presented.	62
The simple and sensitive densitometric method for detection of some hetroaromatic pesticides on TLC plates using 2-trichloro methyl benzimidazole as chromogenic reagent.	Heteroaromatic pesticides	Separation of IAA, IBA, fenpiclonil, ketoconazole and fluconazole by TLC on silica gel coated Al-sheets Visualization was done by 2-trichloro methyl benzimidazole spectrodensitometry was used for quantitative estimation.	63
The detection of some pesticides by the mixed chromatographic enzymic procedure.	Pesticides	Considerable lowering of the detection limit is achieved when cholinesterase inhibition is used with TLC.	64

62. K. Burger, *Duennschicht-Chromatogr.*, 1996, 31-52.
63. L. Konopski and T. Potocka-Smolka, *Pestycydy (Warsaw)*, 1997, **(1-2),** 33-38.
64. M. Staicu and M. Stanculescu, *Sci. Technol. Environ. Prot.*, 1997, **4,** 105-113.

Title	Analyte	Remarks/Comments	Ref.
Chemometric characterization of R_F values of pesticides for TLC systems of the type silica + weakly –polar dilutent –polar modifier.	Pesticides	Determination of relationship between R_F values and mobile phase composition for moderately polar pesticides in systems of the type silica + non polar or weakly polar diluent (heptane or chloroform) – polar modifier (Et acetate, THF, dioxane or acetone). Curvilinear or S-shaped plots are obtained. Low R_F indicates strong adsorption of pesticides and high R_F indicates desorption.	65
Importance of soil map detail in predicting pesticide mobility in terrace soils.	Pesticides	Determination of the most appropriate level of soil map detail for predicting pesticide mobility in terrace soils. Soil TLC was used to measure the relative mobility (R_F) of bench mark pesticides (alachlor, atrazine, carbofuran and dicanba) in samples from each soil core.	66
Optimization of chromatographic separation of pesticides.	Pesticides	The optimization of chromatographic separation of a pesticide mixture using Windows diagram method. Pesticides are separated on RP-18 silica gel thin layers using the solvent system methanol-water as developer. The optimal separation of pesticide mixture was achieved by changing the composition of mobile phase.	67
Online coupling of liquid chromatography with thin layer chromatography.	Pesticides	Online coupling of HPLC and TLC represents a very promising 2D-technique. It allows the combination of two completely different separation principles. Typical applications are pesticide residue analysis in food stuffs and environmental samples.	68

65. E. Soczewinski, T. Tuzimski and K. Pomorska, *J. Planar Chromatogr. –Mod. TLC*, 1998, **11**, 90-93.
66. N. B. Stolpe, M. S. Kuzila and P. J. Shea, *Soil Sci.*, 1998, **163**, 394-403.
67. S. Babic, M. Petrovic and M. Kostelan-Macan, *Kem. Ind.*, 1998, **47**, 275-279.
68. H. J. Stan and F. Schwarger, *J. Chromatogr., A*, 1998, **819**, 35-44.

Title	Analyte	Remarks/Comments	Ref.
Pesticide residues in fruits at market.	Pesticides	A jCS-930 thin layer scanner (TLC scanner) for the determination of pesticide residues (mainly parathion) with TLC plate GF254. Developing agents were 3:1:1 hexane-ethanol-acetone and 1:1 cyclohexane-chloroform.	69.
Quantitative evaluation of 2D chromatograms with a CCD camera.	Pesticides	Separation of mixture of pesticides by two dimensional development on cyano HPTLC plates with a polar mobile phase (hexane-diethyl ether) in 2^{nd} dimension Chromatograms were recorded with a sensitive colour CCD camera and evaluated with Camag Video Scan Software.	70.
Identification of some new pesticides in biological material.	Pesticides	Evaluation of established visualization procedures (UV, Dragondroff reagent, Marquis reagent, Mandlin reagent, H_2SO_4 etc) for the characterization of pesticides by TLC of extracts from biological samples. Sensitivity of the method was 0.5-1.5 mg% depending upon the pesticide.	71.
Recent advances in thin layer chromatography of pesticides.	Pesticides	Advances in the use of TLC and HPTLC for separation, detection and qualitative and quantitative determination of pesticides, other agrochemicals and related compounds are reviewed for the period 1996-1998.	72.

69. Z. Huang and H. Yao, *Nongyao Kexue Yu Guanli*, 1998, **19,** 9-10.
70. M. Petrovic, M. Kastelan-Macan and S. Babic, *J. Planar Chromatogr. –Mod. TLC*, 1998, **11,** 353-356.
71. E. B. Muzhanovsky, A. F. Fartushnyi and A. P. Sukhin, Sud. *–Med. Ekspert.*, 1998, **41,** 20-22.
72. J. Sherma, *J. AOAC Int.*, 1999, **82**, 48-53.

Title	Analyte	Remarks/Comments	Ref.
Thin layer chromatographic detection of pesticide residues in textiles.	Pesticides	Development of simple and easy TLC method for the detection of organic pesticides in textile mills. Pesticides were evaluated and their R_F values were determined. Biocides containing halogen atoms were detected with $AgNO_3$ solution and irradiation with UV light. P-and S-based pesticides were detected by enzymic tests. Limits of detectability was also determined.	73
HPTLC determination of pesticides and PCB'S in cosmetic products.	Polychlorinated biphenyls (PCB'S) organochlorinated pesticides and organophosphate pesticides.	HPTLC analysis procedure to detect the PCB's, pesticides and their mixtures in cosmetics as a preliminary screening to GC determination is one of the most suitable methods for identify and quantify of pesticides and PCB's.	74
Chemometric characterization of the R_F values of pesticides for thin layer chromatographic systems of the type silica + weakly polar dilueut – polar modifier. Part II.	Pesticides	Determination of plots of R_F against mobile phases for pesticides in systems of the type silica – heptane + polar modifier (Et acetate, THF or dioxane).	75

73. H. Bodner and W. Schindler, *Melliand Textilber.*, 1999, **80**, 195-197.
74. C. Neuhoff, C. Villa and S. Dorato, *Acta Technol. Legis Med.*, 1997, **8**, 161-167.
75. E. Soczewinski and T. Tuzimski, *J. Planar Chromatogr. –Mod. TLC*, 1999, **12**, 186-189.

Title	Analtyte	Remaks/Comments	Ref.
Quantitative determination of pesticides in soil by thin layer chromatography and video densitometry.	Propham, chloropropham, atrazine, diflubenzuron, tetramethrin and α-cypermethrin.	RP-TLC in conjunction with video densitometry for determination of mixture of pesticides. Excellent separation was achieved using methanol-water solvent system. Video densitometeric quantification was validated for linearity, precision and detection limit.	76
Soil thin layer chromatography and pesticide mobility through soil microstructures. New technical approach.	Labeled pesticides	Use of 11 different micro structural soils to study the mobility of pesticides. A new correlation i.e. $M = W_R R_F$, where M is pesticide movement, W_R is the rate of water movement and R_F is the retardation factor was proposed to understand the pesticide movement through soil layer under the action of rain.	77
Thin layer chromatographic behaviour of organophosphate pesticides on hydrated stannic oxide layers.	Organophosphate pesticides	A TLC approach based on the use of hydrated stannic oxide as stationary phase. Rapid separation was carried out using various solvent systems. R_F values were related to the polarity of solvent used and to interaction of the compounds with stannic oxide.	78
Thin layer chromatographic method for detection and identification of carbyl, propoxur and carbofuran by use of 4-aminoantipyrine.	Carbyl, propoxur, and carbofuran.	4-amino antipyrine for TLC detection and identification of insecticides is simple, sensitive and can be routinely used in forensic casework.	79

76. P. Ravenel, M. H. Liegeosis, D. Chevallier and M. Tissut, *J. Chromatogr., A,* 1999, **864,** 145-154.
77. M. Petrovic, S. Babic and M. Kastelan-Macan, *Croat. Chem. Acta*, 2000, **73,** 197-207.
78. J. P. Rawat and M. Bhardwaj, *Orient. J. Chem.*, 2000, **16**, 53-58.
79. M. T. Sevalkar, V. B. Patil and M. V. Garad, *J. Planar Chromatogr. –Mod. TLC*, 2000, **13,** 235-237.

Title	Analyte	Remarks/Comments	Ref.
Chemometric characterization of the R_F values of pesticides for thin layer chromatographic systems of the type silica-non polar modifier. Part III.	pesticides	Analysis of pesticides by TLC in rapid non-aqueous systems of the type silica-heptane + polar modifier (Et acetate, THF, dioxane or disopropyl ether). The greatest spread of points, indicative of individual selectivity, was obtained for aqueous mobile phases and octadecyl silica adsorbent wettable with water (RPW18).	80
Assessment of pesticide mobility by packed soil columns and soil thin layer chromatography.	Pesticides	Examination of leaching pattern of pesticides by soil packed column chromatography and soil TLC.	81.
Assessment of the movement of pesticides by soil thin layer chromatography using successive elutions.	Fungicides	Assessment of the movement of pesticides by soil TLC using successive elution. Visualization of radiolabeled compounds using linear detector and autoradiography on glass plates layered with a fine soil fraction (sieved at 100 μm) having layer thickness 250 μm.	82.
Mobility assessment of hydrophobic pesticides in the surfactant-soil-water system.	Pesticides	Method to investigate the interaction of surfactants with soil-water partitioning of hydrophobic pesticides at doses below and above the surfactant critical micellar concentration.	83.

80. T. Tuzimski and E. Soczewinski, *J. Planar Chromatogr. –Mod. TLC*, 2000, **13,** 271-275.
81. E. Griessbach, R. Deleu and A. Chopin, *Pestic./Soil Interact. J. Cornejo*; P. Jamet (eds.), 2000, 49-55.
82. D. Hoyoux-Roche, Pestic./Soil Interact., *J. Cornejo; P. Jamet* (eds.), 2000, 57-63.
83. A. B. P. Parez and B. R. M. S. L. Rahman, *Pestic./Soil Interact., J. Cornejo*; P. Jamet (eds.), 2000, 65-74.

Title	Analyte	Remarks/Comments	Ref.
Application of the thin-layer chromatography for the study of pesticide mobility in soils.	Radioactive pesticides	Determination of radioactive pesticides using linear analyzer to obtain both linear chromatograms and precise images in two or three dimensions of the spots on the plate.	84.
Soil thin-layer chromatography.	Pesticides	Investigation of migration behaviour of active pesticide ingredients on soil layer using water as mobile phase and their identification applying physico-chemical detection methods.	85.
An availability test of pesticides from soils.	Pesticides	Classification of pesticides according to their adsorption, desorption intensity, sensitivity towards mobility and behaviour in the plant-soil-water environment. The interactions between pesticides and soil in relationship with soil properties (% of organic carbon and pH).	86.
Methods for determination of pesticide adsorption on soils and their constituents.	Pesticides	Simple and useful method to obtain a wide information about the adsorption of pesticides or other organic compounds by different adsorbents (soil, peat, clay minerals etc.), the effect of temp on this process the exchange cations characteristics and the dominating bonding mechanisms, under laboratory conditions.	87.
Quantitative determination of pesticides in soil by thin-layer chromatography and video densitometry.	Pesticides	Use of reversed phase TLC in conjunction with video densitometry for the determination of a six component mixture of pesticides. Methanol-water solvent systems were used for achieving separation of probham, chlorpropham, atraznie, diflubenzuron, tetramethrin and α-cypermethrin.	88

84. M. J. Sanchez-Martin and M. Sanchez-Canazano, *Pestic./Soil Interact, J. Cornejo*; P. Jamet (eds.), 2000, 75-82.
85. W. Steurbaut and L. Pussemier, *Pestic./Soil Interact., J. Cornejo*; *P. Jamet (eds.)*, 2000, 83-87.
86. R. Deleu and A. Copin, *Pestic./Soil Interact. J. Cornejo*; P. Jamet (eds.), 2000, 179-184.
87. E. Romero Taboada, G. D. Cancela, A. P. Herax and F. Sanchez-Rasero, *Pestic./Soil Interact., J. Cornejo*; P. Jamet (eds.), 2000, 197-205.
88. M. Petoric, S. Babic and M. Kastelan-Macan, *Croat. Chem. Acta*, 2000, **73,** 197-207.

Title	Analyte	Remarks/Comments	Ref.
Thin-layer chromatographic studies of the mobility of pesticides through soil containing static flat-beds.	Pesticides	Study of chromatographic behaviour of some pesticides on silica, soil and mixed layers containing soil, with aqueous ammonia or sodium salt solutions, with or without added N-cetyl-N, N, N-trimethyl ammonium bromide (CTAB). Intresting aspect of this study is migration of pesticides such as phosphamidon and dimethoate through pure soil.	89.
Analysis of pesticide residues in tomato by TLC.	Pesticides (Atrazine, diuron, chloroxuron, metribuzin).	Detection of pesticide residues using the Hill reaction. Pesticides were applied on silica gel plates with a microsyringe. Elution was done with Et acetate. The range of the detected concentrations was from 0.1 to 1.0 ng/µl. Semi-quantitative analysis can be made using the results.	90
Examination of the pesticide residue of organophosphates and carbamates on the spot by thin layer chromatography.	Organophosphate and carbonate pesticides	Examination of organophosphate and carbamate pesticides by TLC with the acetylcholinesterase inhibition in vegetables, fruits and foods. This method can identify pesticides from 0.5 to 1.0 µg/ml.	91
Thin layer chromatographic separation of some common pesticides on mixed stannic oxide-silica gel G layers.	Organophosphorus organochlorine, pyrethroid pesticides	TLC of 14 important organophosphorus organochlorine and pyrethroid pesticides on mixed stannic oxide-silica gel G layers. Variety of mixed aqueous and organic mobile phases were used. R_F values were determined. Several important and difficult separations of synthetic pesticide mixtures were achieved.	92

89. A. Mohammad, I. A. Khan and N. Jabeen, *J. Planar Chromatogr. –Mod. TLC*, 2001, **14**, 283-290.
90. S. L. Moraes, M. O. O. Maria, L. E. Nakagawa and L. C. Luchini, *Quimica Nova* 2002, **25,** 196-202.
91. J. Z. Zhao, Z. J. Fan, J. An, X. F. Yan, G. Z. Liang and Z. Y. Wang, *Sichuan Shifan Daxue Xue-bao, Ziran Kexueban*, 2001, **24,** 496-498.
92. S. A. Nabi, A. Gupta, M. A. Khan and A. Islam, *Acta Chromatogr.*, 2002, **12,** 201-210.

Title	Analyte	Remarks/Comments	Ref.
Chemometric characterization of the R_F values of pesticides in thin-layer chromatography on silica with mobile phases comprising a weakly polar diluent and a polar modifier. Part IV.	Pesticides	Plots of R_F against modifier concentration, C_{mod}, are reported for 31 moderately polar pesticides in systems of the type silica-hepane + modifier (Et acetale, THF, and dioxane.).	93
Use of database plots of pesticide retention (R_F) against mobile phase composition. Part I. Correlation of pesticide retention data in normal and reversed phase systems and their use to separate a mixture of 10 pesticides by 2D TLC.	Pesticides	Separation of 10 pesticides by 2D development on TLC plates coated with coupled layers of octadecyl silica (reversed-phase, RP) and plain silica (normal-phase, NP). Binary mobile phases aq-org. for RP chromatography and nonaq. for NP chromatography were chosen.	94
Use of database plots of pesticide retention (R_F) against mobile phase composition. Part II. TLC is a pilot technique for transferring retention data to HPLC, and use of the data for preliminary fractionation of a mixture of pesticides by micro preparative column chromatography.	Pesticides	Determination of relations between R_F values and mobile phase composition for moderately polar pesticides in NP systems silica-non polar diluent (heptane)-polar modifier (Et acetate, THF or dioxane) and in RP system of the type octadecyl silica-water-polar modifier (acetonitrile, methanol or THF.).	95

93. T. Tuzimski, *J. Planar Chromatogr. –Mod. TLC*, 2002, **15,** 124-127.
94. T. Tuzimski and E. Soczewinski, *Chromatographia.* 2002, **56,** 219-223.
95. T. Tuzimski and E. Soczewinski, *Chromatographia*. 2002, **56,** 225-227.

Title	Analyte	Remarks/Comments	Ref.
Determination of harmful substances in foods-effect-related analysis, a new concept for pesticide detection.	Fungicides and insecticides	Combination of HPTLC of organic food pollutants with toxicity testing using the same chromatogram for a bioassay including image analysis. A method is described concerning post chromatographic detection of fungicides by Penicillium and insecticides by cholinesterase in different plant products.	96
Combined thin layer chromatography for the screening of pesticides in samples derived from biological origins.	Pesticides	Method for off-line coupling of TLC with electron impact ionization (EI) –mass spectrometry for routine determination of pesticides in toxicology and forensic medicine. Six TLC solvent systems are described for 151 different pesticides. 8-peak mass-spectra generated from full EI mass spectra are listed.	97
Fluorescence screening of organophosphorus pesticides in water by an enzyme inhibition procedure on TLC plates.	Organophosphorus pesticides	An enzymic inhibition method sufficiently sensitive for rapid screening of 7 OPP in H_2O. Pesticides were separated on silica gel TLC plates with n-hexane-acetone, 75+30 (vol/vol.) as mobile phase. An enzymic anal. technique on TLC plates was developed using 7-diethylamino-3-(4'-maleimidyl phenyl)-4-methyl coumarin (maleimid CPM) as fluorogenic reagents. Limit of detection was 1-10 ng/spot.	98

96. C. Weins and O. Collet, *Lebensmittechemie*, 2002, **56,** 128-131.
97. H. Brzezinka and N. Bertman, *J. Chromatogr. Sci.*, 2002, **40,** 609-613.
98. M. Hamada and R. Wintersteiger, *J. Planar Chromatogr. –Mod. TLC*, 2003, **16,** 4-10.

Title	Analyte	Remarks/Comments	Ref.
Multiresidue screening methods for determination of pesticides in tomatoes.	Pesticides	Investigation of the possibilities of applying TLC detection for the analysis of pesticide residues in tomatoes. Silica gel plates were used as stationary phase. Pesticides were eluted with Et acetate and dichloromethane. Two eluting solvent systems were tested, one using the reagents O-toluidine + potassium iodide (O-TKI) and the other p-nitrobenzene fluoroborate (NBFB). Limit of detection were measured for semi quantitative analysis.	99
Correlation of retention data of pesticides in normal and reversed phase systems and utilization of the data for separation of a mixture of ten urea herbicides by two dimensional thin layer chromatography on cyanopropyl bonded polar stationary phase and on a two adsorbent layer multi-KSC5 plate.	Herbicides	Comparision of the selectivities of TLC systems by use of correlation between R_F (II) and R_F (I) values (by analogy with 2D-TLC). The greatest individual selectivity was obtained with following combinations : non-aq. mobile phases comprising a weakly polar diluent (heptane) and a polar modifier (THF) on silica and for aq. mobile phases comprising a polar solvent (methanol) in water-wettable octadecyl silica (RP-18W).	100

99. S. L. Moraes, M. O. O. Rezende, L. E. Nakagawa and L. C. Luchini, J. Env. Sci. and Health, Part B: Pesticides, *Food Contaminants and Agricultural Wastes* 2003, B **38,** 605-615.
100. T. Tuzimski and E. Soczewinski, *J. Planar Chromatogr. -Mod. TLC*, 2003, **16,** 263-267.

Title	Analyte	Remarks/Comments	Ref
HPTLC/AMD in water analysis determination of hydroxylated triazine decomposition products and acidic pesticides.	Hydroxylated triazine decomposition. Products and acidic pesticides.	The trace analysis of polar water pollutants in surface water samples by using HPTLC/AMD technique. Comparision is made with HPLC-MS.	101
Thin-layer chromatography: a simple and reliable technique for the determination of pesticide residue in environmental samples.	Pesticides	A method for detection of pesticides by TLC. Pesticides on chlorination and treatment with O-toluidine, yield on intensively coloured blue product. Organophosphates and carbamates can be detected at low level (μg/g). The limit of detection is 10-100 ng.	102
Separation of a mixture of pesticides by 2D-TLC on two-adsorbent layer multi-KSC5 plate.	Pesticides	2D-TLC for the separation of a mixture of pesticides. The correlations of R_F values in NP/RP systems were utilized in the practical separation of a mixture of pesticides using 2D-TLC on a Multi-KSC5 plate. The plates were scanned and videos canned.	103
Determination of pesticides in honey by ultrasonic solvent and thin-layer chromatography.	Atrazine and simazine	A rapid method for quantitative determination of atrazine and simazine in honey. Extraction of pesticides was done with benzene : water = 1:1 (vol./vol.) mixture. The appenent recovery of pesticides from honey was 92.3 ± 2.4 for atrazine and 94.2 ± 2.8 for simazine.	104

101. R. Albert and W. Weber, *CLB Chemie in Labor und Biotechnik*, 2004, **55,** 172-175.
102. M. R. Asi, A. Hussain and Z. Iqbal, *Pak. J. Anal. Chem.* 2000, **1**, 10-13.
103. T. Tuzimski and J. Wojtowicz, *J. Liq. Chromatogr. and Rel. Technol.*, 2005, **28,** 277-287.
104. I. Rezic, A. J. M. Horvat, S. Babic and M. Kastelan-Macan, *Ultrasonics Sonochem.*, 2005, **12**, 477-48.

Title	Analyte	Remarks/Comments	Ref.
Two stage fractionation of a mixture of 10 pesticides by TLC and HPLC.	Pesticides	Determination of relationships between R_F values and mobile phase composition for 10 pesticides in NP systems. Optimum systems for preliminary fractionation of pesticides by zonal micropreperative TLC were chosen. Preparative separation of the complex mixture by TLC on silica (non aq. eluent, NP systems), combined with TLC or/and HPLC (aq. eluent, RP system) or HPLC (NP system), gives good perspective of full separation of the simpler fraction in the second stage.	105
HPTLC determination of imidacloprid, fenitrothion and parathion in Chinese cabbage.	Imidacloprid, fenitrothion, and parathion.	A simple rapid and sensitive HPTLC method validated for the analysis of residues of imidacloprid, fenitrothion and parathion in Chinese cabbage. Extraction was done with acetone-petroleum ether, 5:3 (vol./vol.). Stationary phase used was silica gel $60F_{254}$ HPTLC plates; hexane-acetone, 7+3 (vol./vol.) was used for plate development. R_F values, detection limits, recoveries and RSD were determine.	106
Two stage fractionation of a mixture of pesticides by micropreparative TLC and HPLC.	Pesticides	Preliminary fractionation by zonal micro preperative TLC by applying pesticides to the edge of the layer in 'frontal + elution' mode. Preparative separation of the complex mixtures by TLC on silica (non-aq. mobile phase, NP system) combined with TLC or HPLC (aq. mobile phase, RP system) results in the strong possibility of full separation of the simpler fractions in the second stage by use of the two independent methods.	107

105. T. Tuzimski, J. *Liq. Chromatogr.* and *Rel. Technol.*, 2005, **28,** 463-476.
106. H. Cao, Y. Yue, R. Hua, F. Tang, R. Zhang, W. Fan and H. Chen, *J. Planar Chromatogr. -Mod. TLC*, 2005, **18,** 151-154.
107. T. Tuzimski, *J. Planar Chromatog. -Mod. TLC*, 2005, **18,** 39-43.

Title	Analyte	Remarks/Comments	Ref.
Use of genetic algorithm to optimize TLC separation.	Pesticides	Method for optimization of a TLC separation based on the use of a genetic algorithm. The procedure was tested by optimization of the RP-HPTLC separation of a mixture of 6 pesticides. The performance was tested by measurement of the no. of generations, the population size the mutation probability and crossover probability. Three separation criteria (MRF, R* and R**) were examined as fitness functions. Comparison with Simplex method.	108
Study of quantitative structure-retention relationships for S-triazine derivatives in different RP HPTLC systems.	S-triazine pesticides	QSSR to study the chromatographic behaviour of some S-triazine pesticides. Variety of partition coefficients were calculated. Correlation between partition coefficients and chromatography obtained lipophilicty was analysed. C_{18} layers with methanol-water as mobile phase was selected as the best RP-HPTLC system for determination of the octanol/water partition coefficient and the lipophilicity of the molecules.	109
Application of thin-layer chromatography in analysis of selected plant protection products.	Roadenticides.	Application of TLC in quantitative analysis of plant protection products. Samples of rodenticides containing coumatetralyl, and formulations containing propiconazole, trifloxystrobin, flurasulam and triforine were analysed. Examinations for active ingredients belonging to the group of plant growth regulators like 1-NAA and gibrellic acid were also performed.	110

108. S. Babic, A. J. M. Horvat and M. Kastelan-Macan, *J. Planar Chromatogr., -Mod. TLC*, 2005, **18,** 112-117.
109. N. U. Perisic-Janjic, T. L. Djakovic-Sekulic, L. R. Jevric and B. Z. Javanovic, *J. Planar Chromatogr. -Mod. TLC*, 2005, **18,** 212-216.
110. A. Silowiecki and S. Dudkowska, *Progress in Plant Protection*, 2004, **44**, 1086.

Title	Analyte	Remarks/Comments	Ref.
Application of TLC for confirmation and screening of pesticide residues in fruits, vegetables and cereal grains: Part 2. Repeatability and reproducibility of R_F and MDQ values.	Pesticides	A review illustrates the effect of major factors influencing the reproducibility of TLC separation and detection under largely differing environmental and laboratory conditions.	111
Standardization and application of TLC-enzyme inhibition method for detection of organophosphate and organocarbamate pesticides in model mixture.	Organophosphate and organocarbamate pesticides	A simple, rapid and sensitive TLC-EI method for the separation of model mixture of 8 OPP and 1 OCP. Best resolution was achieved with precoated TLC aluminium sheet (20 cm x 20 cm) of aluminium oxide 60 F_{254} neutral type E (200 μ) with the solvent system acetone : hexane (30:70 vol./vol.) at 25° C. Detection limits were also measured.	112
Application of TLC in multiresidue methods for the determination of pesticides in wheat grain.	Pesticides	Comparison of 3 TLC detection methods in combination with Et acetate extn. and gel permeation chromatography clean-up method for screening pesticides residues in wheat grains. Visualization is done by chemical reagent (O-tolidine + KI, photosynthesis inhibition by Hill detection method, AlO_3 G incorporated with $AgNO_3$ + UV exposition.).	113

111. A. Arus, I. Fuezesi, J. Lantos, I. Korsos, M. Szathmary and T. Hatfaludi, J. Environ. Sci. and Health, Part B : Pesticides, *Food Contaminants and Agricultural Wastes*, 2005, **B40**, 485-511.
112. P. K. Nair and B. K. Wadhwa, *Ind. J. Dairy Sci.* 2004, **57**, 238-240.
113. O. Tiryaki and P. Aysal, Bulletin of Environ. *Contamination and Toxicol.* 2005, **75**, 1143-1149.

Title	Analyte	Remarks/Comments	Ref.
Use of thin-layer chromatography in combination with diode-array scanning densitometry for identification of fenitrothion in apples.	Fenitrothion	TLC in combination with fiber optical (diode array) scanning densitometry for identification of fenitrothion in apples and fresh apple juice. The technique enabled parallel recording of chromatograms and *in-situ* UV-Visible spectrometry in the range X = 191-612 nm.	114
Thin-layer chromatographic methods for the analysis of eighteen different ^{14}C-labeled pesticides.	^{14}C-labeled pesticides	TLC methods were used in a major survey of pesticide persistence in the environment as a preliminary tool for selection of compounds for further investigation by HPLC and GC. ^{14}C-labeled metabolites were included to ensure separation of the parent compounds from their known metabolites.	115
Rapid screening of water by TLC-bioluminescence.	Toxins and adulterants (including pesticides)	Bioluminex is a kit system designed for multiplex detection of toxins and adulterants in complex mixtures. It involves direct coupling of bioluminescence detection of TLC. HPTLC plates coated with luminescent Vibrio fischeri were used and results recorded using a dark box and cooled CCD camera systems.	116

114. T. Tuzimski, *J. Planar Chromatogr. -Mod. TLC*, 2005, **18,** 419-422.
115. J. Rusmussen and O. S. Jaconseb, *J. Planar Chromatogr. -Mod. TLC*, 2005, **18**, 248-251.
116. S. M. Verbitski, G. Gourdin, L. Ikenoye and J. D. Mc-Chesney, Reprints of Extended Abstracts Presented at the ACS National Meeting, Am. Chem. Soc., Division of Environ. Chem. (Computer optical disk), 2005, **45,** 180-183.

Title	Analyte	Remarks/Comments	Ref.
Thin-layer chromatography of pesticides-A review of applications for 2002-04.	Insecticides, herbicides and fungicides	Applications of TLC and HPTLC for the separation, detection and qualitative and quantitative determination of pesticides, other agrochemicals and related compounds are reviewed for the period 2000-04. Topics like structure relationships, metabolism, degradation, adsorption, uptake dissipation, mobility and lipophilicity of pesticides are also covered.	117
Thin layer chromatography for selective detection of methomyl in forensic casework.	Carbamate insecticide (methomyl)	Phloroglucinol a rapid specific and sensitive reagent for detection of the carbamate insecticide methomyl in toxicological analysis by TLC. The recovery of methonyl was 75%. Phloroglucinol is recommended for the selective detection and semi-quantitative determination of methomyl in biological samples.	118
Application of thin-layer chromatography in food anlaysis. Part 2. Application examples.	Pesticides	TLC/HPTLC, alongside GC and HPLC is a complementary or confirmative method in food analysis. Fast identity and purity tests with quantitative results w.r.t. undesired substances in food and feed stuffs.	119

117. J. Sherma, *Acta Chromatographica* 2005, **15**, 5-30.
118. R. S. Mali, B. D. Dhongade, R. R. Kulkarni and V. S. Pandav, *J. Planar Chromatogr. –Mod. TLC*, 2006, **19**, 85-86.
119. K. Zieloff and M. Werther, *Deutsche Lebensmittel-Rundschau* 2006, **102**, 24-27.

REFERENCES:

[1]. L. S. Ettre. Nomenclature for Chromatography (IUPAC Recommendation 1993), *Pure Appl. Chem.*, 1993, **65**, 819.

[2]. F. F. Runge. Zur Farbenchemic. Muster bilder fiir Freundedes Schonen und zum Gebrauch fiir Zeichner, Maler, Verzierer und Zeugdrucker, Berlin, 1850.

[3]. F. F. Runge, Der Bildungstriebe der Stoffe, veranschauchlicht in selbstandig gewachsenen Bildern, Oranienburg, 1855.

[4]. H. Weil and T. I. Williams, *Naturwissenschaftern*, 1953, **40**, 1-7.

[5]. L. S. Ettre, Evolution of Liquid Chromatography, in Cs. Horvath (Ed.), High Performance Liquid Chromatography. Advances and Perspectives, Academic Press, New York, 1980, **1**, 2-74.

[6]. N. A. Ismailov and M.S. Schraiber, *Farmatsiya (Sofia),* 1938, **3**, 1.

[7]. M. S. Schraiber, *J. Chromatgr.*, 1972, **73**, 367-370.

[8]. F. Kreuzig, *J. Planar Chromatogr.*, 1998, **11**, 322-324.

[9]. J. E. Meinhard and N. F. Hall, *Anal. Chem.*, 1949, **21**, 185-188.

[10]. J. G. Kirchner and G. J. Keller, *J. Am. Chem. Soc.*, 1950, **72**, 1867-1868.

[11]. E. Stahl, *Pharmazie.*, 1956, **11**, 633-637.

[12]. E. Stahl, *Chem. Z.,* 1958, **82**, 323-329.

[13]. E. Stahl (Ed.) Dunnschicht-Chromatographic. Ein Laboratoriums-handbuch, Springer, Berlin, 1962.

[14]. H. Kalasz, L. S. Ettre and M. Bathori, *LC-GC Magazine*, 1997, 1044-1050.

[15]. M. W. Beyerink and R. L. M. Synge, *Biochem., J.,* 1941, **35**, 1358.

[16]. H. P. Wijsman, D. De Beshouwdals, Mengsel Van, Mattase en Dentrinase Amsterdam, 1898.

[17]. H. Jork, W. Funk and H. Wimmer, Physical and Chemical Detection Methods: Fundamentals, Reagents I : Thin-Layer Chromatography

Reagents and Detection Methods, Vol. 1a; VCH Verlages-gesellschaft; Weinchein, FRG, 1990, 464.

[18]. N. Fatima and A. Mohammad, *Sepn. Sci. Technol.*, 1984, **19**, 429.

[19]. A. Mohammad and N. Fatima, *Chromatographia,* 1986, **22**, 109.

[20]. A. Mohammad and S. Tiwari, *Microchem. J.*, 1991, **44,** 39.

[21]. N. V. K. Nanda and Y. P. Devi, *J. Assoc. Office. Anal. Chem.*, 1981, **64,** 729.

[22]. J. Maslwaska and Z. Mlodzikowski, *Chem. Anal.*, 1986, **31**, 193.

[23]. R. Kuroda and K. Oguma, *Anal.Chem.* 1967, **39,** 1003.

[24]. R. Kuroda, N. Kojima and K. Oguma, *J. Chromatogr.*, 1972, **69**, 223.

[25]. K. Oguma, *J. Chromatogr.*, 1969, **42**, 96.

[26]. K. Oguma, *Talanta*, 1969, **16,** 409.

[27]. K. Oguma and R. Kuroda, *J. Chromatogr.*, 1970, **52,** 339.

[28]. K. Oguma and R. Kuroda, *J. Chromatogr.*, 1971, **61**, 307.

[29]. K. Oguma, K. Sato and R. Kuroda, *Chromatographia*, 1993, **37,** 319.

[30]. Y. Q. Feng, M. Shibakawa and K. Oguma, *Chromatographia,* 1995, **41,** 532.

[31]. K. Oguma; K. Inove; Y. Fujinaga; K. Yokota; T. Watanable; T. Ohyama; K.Takeshi and K. Inove. *J. Toxicol. Toxin Rev*, 1999, **18**, 17.

[32]. R. Bhushan and S. Joshi. Int. *J. Bio-Chromatogr.*, 1998, **4**, 95.

[33]. R. Bhushan and R. Agrawal. *Biomed. Chromatogr.*, 1998, **12,** 322.

[34]. J. Sherma. *Anal. Chem.*, 9 R 2000, 72.

Chapter – 2

Thin Layer Chromatography of Pesticides, Metal Ions and Surfactants

2.1 INTRODUCTION

Flat bed or planar chromatography has been considered as one of the simplest analytical technique with general efficiency for the separation of organic and inorganic substances [1-6]. The convenience and cost effectiveness of thin-layer chromatography (TLC) have resulted in its wide range of applicability in separation and identification of agrochemicals [7-13] including pesticides, metal ions and surfactants. In fact TLC and HPTLC techniques complement the other more sensitive and precise primary methods (eg GLC, HPLC, SFC and capillary electrophoresis) used for the analysis of agrochemicals.

Soil provides us a place to live and is a reservoir of minerals but with accelerating growth of world's population and rapid urbanization tremendous pressure has been created on it. Insecticides, herbicides and health protection are very potent pollutants having long range effects and their indiscriminate use poses a serious danger to structure and function of the ecosystems. Pesticides while eliminating the beneficial insects may cause ecological inbalance. At the same time they are phytotoxic and destroy useful plants. They enter the food chain causing toxicity to human beings, animals and other creatures. Many books [14-19] and reviews [20-22] have been published on this subject as a warning of potential hazards.

The major source of metal pollution is the disposal of industrial wastes emenating from metal furnishing (electroplating, metal polishing, metal cleaning etc.) industrial process into the water bodies. Metal pollutants from electroplating operations can find their environmental pathways through air, food, soil and water into plant and animal tissues. Metals tend to get adsorbed easily on surface soils and sediments. Metals in the waste water may be present in the form of metal ions, metal complexes and pure metal particulates.

The analysis of surfactants has assumed importance because of their industrial, commercial and medicinal uses. Surfactants being amphiphilic substance due to the presence of polar and non polar moieties in the same molecule have a broad range applications as cleaning, wetting and emulsifying agents in a variety of industrial and domestic situation. Several analytical techniques have been utilized for quantitative determination of surfactants in different formulations.

Most of the reported TLC methods for the analysis of agrochemicals involve the use of mixed organic solvent systems containing benzene, hexane, chloroform, acetonitrile, ethylacetate or dichloromethane as one of the components. of the layer materials examined, silica gel and alumina have been the most favoured. A few studies have also been reported [7] on the use of barium and calcium sulphate, calcium carbonate and phosphate, soil, cellulose, C_{18} bonded silica gel as layer material to examine the mobility pattern of pesticides. Investigations [23-27] regarding pesticides metabolism in soil and plants, uptake of pesticides by plants from soil and pesticides migration in soil by TLC indicate that soil TLC has much to offer to the chemists interested in examining the uptake, translocation and degradation of pesticides in the environment.

A new concept of qualitative analysis by soil TLC was developed by Helling and Turner in 1968 [28]. Their method was utilized by several workers to examine the mobility pattern of pesticides [29-32] and heavy metals [33-38] in various types of soils. An interesting study on mobility of cadmium on twenty-two soil layers of different nature has been reported by M- Sanchez Camazano and M. J. Sanchez-Martin [39]. Their results clearly demonstrate the significant influence of the soil properties on the mobility of cadmium.

As usual practice, silica gel has been frequently used as stationary phase for the separation of pesticides, metal ions and surfactants followed by the use of alumina, kieselguhr, cellulose and other adsorbents. TLC methods reported so for investigating the mobility of agrochemicals in soil did not consider much the effect of silica in soil bed.

In view, of the above fact, it was considered worthwhile to examine the mobility of agrochemicals (pesticides, heavy metal ions and surfactants) through static planar soil bed amended with silica in different ratios and using appropriate mobile phases. The results of this study may be of immense utility to understand the mobility or leachability of agrochemicals through pure and soil amended layers. The mobility or leachability of such agrochemicals through the soil bed has tremendous influence on the life process of plants.

2.2 EXPERIMENTAL

All experiments were performed at 30 ± 5 °C.

Apparatus

A thin layer chromatography applicator (Toshniwal, India), 20 x 3.5 cm glass plates and 24 x 6 cm glass jars were used.

Reagents

Silica gel G (Merck, India), tetradecyl trimethyl ammonium bromide (Merck, India), cetyl pyridinium chloride, N-cetyl-N, N, N-trimethyl ammonium bromide, Cween 20, Cween 40, Cween 60 (CDH, India), hexadecyl trimethyl ammonium bromide, Brij 58, Brij 78 (Aldrich, Germany), Brij 35, Tween 20 (LOBAS Chemie), Triton-X 100 (Rohm & Haas Company), methyl parathion, malathion, dichlorovos, dimethoate, chloropyrifos, ziram (Bayer, India). All other reagents (sodium chloride, dimethyl sulfoxide, acetone etc.) used were also of Analytical Reagent grade.

Agrochemicals Studied

Surfactants

Triton-X100 (TX-100), Brij 35 (BJ-35), Brij 57 (BJ-57), Brij 78 (BJ-78), Brij 98 (BJ-98), Tween 20 (TW-20), Cween 20 (CW-20), Cween 40 (CW-40), Cween 60 (CW-60), cetyl pyridinium chloride (CPC), cetyl trimethyl ammonium bromide (CTAB), tetradecyl trimethyl ammonium bromide (TTAB), hexadecyl trimethyl ammonium chloride (HDTAC), dodecyl trimethyl ammonium bromide (DTAB).

Pesticides

Methyl parathion (MLPN), malathion (MLN), dichlorovos (DCVS), dimethoate (DMT), chloropyrifos (CLPS), ziram (ZRM) (See Table 2.1).

Metal Ions

Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Mo^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Cr^{6+}, Cr^{3+}.

Test Solutions

All test solutions of surfactants and pesticides were prepared in methanol. Ziram was prepared in distilled water.

1% standard solutions of the chloride, nitrate, or sulphate salts of the above mentioned metal ions were used.

Soil Sample

We used one sample (S_1) of natural, uncultivated soil that was collected from the soil surface horizon (0-20 cm deep) at Fort in the district of Aligarh (India).

Detectors

(a) For Surfactants

Dragendorff reagent and iodine vapours were used to detect all the surfactants.

Preparation of Dragendorff Reagent:

It was prepared by mixing two solutions A and B.

Solution A: It was prepared by adding two solutions.

(i) Solution of bismuth subnitrate ($BiONO_3.H_2O$; 1.7g) dissolved in acetic acid (20ml) and diluted to 100ml with water.

(ii) Solution of potassium iodide (65g) in water (200ml).

Both solutions were transferred into 1L flask and acetic acid (200ml) was added. The contents were diluted to one liter with water.

Solution B: It was prepared by dissolving barium chloride dehydrate ($BaCl_2.2H_2O$; 290g) in water (1L).

Solution A and B were mixed in the ratio 2:1.

(b) For Metal Ions

- Zn^{2+} and Cd^{2+} were detected with a solution of 0.5% dithizone in carbon tetrachloride.
- Ni^{2+} and Co^{2+} were detected with 1% solution of alcoholic dimethylglyoxime.
- Cu^{2+} and Mo^{2+} were detected with haemotoxylin solution.
- Mn^{2+} was detected with 2M aqueous NaOH in 30% H_2O_2 in 1:1 (vol./vol.)
- Fe^{2+} and Fe^{3+} were detected with 1% potassium ferrocyanide.
- Cr^{6+} and Cr^{3+} were detected with saturated solution of $AgNO_3$ in methanol.

(c) For Pesticides

Iodine vapours were used to detect all the pesticides except one i.e. ziram. Ziram was detected by PAN indicator.

Stationary Phase

The stationary phases used for different analytes are listed in Tables 2.2 (for surfactants), 2.3 (for metal ions) and 2.4 (for pesticides).

Mobile Phase

The mobile phases used for different analytes are listed in Tables 2.5 (for surfactants), 2.6 (for metal ions) and 2.7 (for pesticides).

Table 2.1 IUPAC name, chemical formula and solubility data in water of pesticides used in the present study

Commercial name and abbreviation used	IUPAC name	Chemical formula	Solubility in water (mg/L, 25 °C)
Chloropyrifos (CLPS)	o, o-diethyl o-3, 5, 6-trichloro-2-pyridyl phosphorothioate	$C_9H_{11}C_{13}No_3PS$	ca.2.0
Dichlorovos (DCVS)	2,2-dichlorovinyl dimethyl phosphate	$C_4H_7Cl_{12}O_4P$	ca.10 x 10^3
Dimethoate (DMT)	o, o-dimethyl S-methyl carbomoylmethyl phosphorodithioate	$C_5H_{12}NO_3PS_2$	25 x 10^3
Malathion (MLN)	o, o-dimethyl phosphorodithioate	$C_{10}H_{19}O_6PS_2$	145.0
Methyl parathion (MLPN)	o, o-dimethyl o-4-nitrophenyl phosphorothionate	$C_8H_{10}NO_5PS$	55-60
Ziram (ZRM)	zinc dimethyldithiocarbamate	$C_6H_{12}N_2S_4Zn$	65.0

Data taken from: The agrochemicals handbook (Doughlas Hastley and Hamish Kidd eds.), 2nd edition, royal society of chemistry (England) 1987.

Table 2.2 The stationary phases used for surfactants

Code	Components
Single component stationary phases	
S_1	Soil
S_2	Silica gel
Mixed stationary phases	
S_3	$S_1 + S_2$ (9:1)
S_4	$S_1 + S_2$ (8:2)
S_5	$S_1 + S_2$ (7:3)
S_6	$S_1 + S_2$ (6:4)
S_7	$S_1 + S_2$ (5:5)
S_8	$S_1 + S_2$ (4:6)
S_9	$S_1 + S_2$ (3:7)
S_{10}	$S_1 + S_2$ (2:8)
S_{11}	$S_1 + S_2$ (1:9)

Table 2.3 The stationary phases used for metal ions.

Code	Components
Single component stationary phases	
S_1	Soil
S_2	Silica gel
Mixed stationary phases	
S_3'	S_1 impregnated with 1 x 10^{-3} M
S_4'	S_1 impregnated with 1 x 10^{-5} M
S_5'	S_1 impregnated with 1 x 10^{-3} M
S_6'	S_1 impregnated with 1 x 10^{-5} M
S_7'	S_1 impregnated with 1 x 10^{-4} M
S_8'	S_1 impregnated with 1 x 10^{-4} M
S_9'	S_2 impregnated with 1 x 10^{-3} M
S_{10}'	S_2 impregnated with 1 x 10^{-5} M
S_{11}'	S_2 impregnated with 1 x 10^{-3} M
S_{12}'	S_2 impregnated with 1 x 10^{-5} M
S_{13}'	S_2 impregnated with 1 x 10^{-2} M
S_{14}'	S_2 impregnated with 1 x 10^{-4} M
S_{15}'	$S_1 + S_2$ (2:8) impregnated with 1 x 10^{-3} M
S_{16}'	$S_1 + S_2$ (2:8) impregnated with 1 x 10^{-5} M
S_{17}'	$S_1 + S_2$ (2:8) impregnated with 1 x 10^{-3} M
S_{18}'	$S_1 + S_2$ (2:8) impregnated with 1 x 10^{-5} M
S_{19}'	$S_1 + S_2$ (2:8) impregnated with 1 x 10^{-2} M
S_{20}'	$S_1 + S_2$ (2:8) impregnated with 1 x 10^{-4} M

Table 2.4 Stationary phases used for pesticides.

Code	Components
Single component stationary phase	
S_1	Soil
S_2	Silica gel
Mixed stationary phase	
S''_3	S_1 impregnated with 5% aq. sol. of Zn^{2+}
S''_4	S_1 impregnated with 5% aq. sol. of Cu^{2+}
S''_5	S_1 impregnated with 5% aq. sol. of Cd^{2+}
S''_6	S_2 impregnated with 5% aq. sol. of Zn^{2+}
S''_7	S_2 impregnated with 5% aq. sol. of Cu^{2+}
S''_8	S_2 impregnated with 5% aq. sol. of Cd^{2+}
S''_9	$S_1 + S_2$ (8:2) impregnated with 5% aq. sol. of Zn^{2+}
S''_{10}	$S_1 + S_2$ (8:2) impregnated with 5% aq. sol. of Cu^{2+}
S''_{11}	$S_1 + S_2$ (8:2) impregnated with 5% aq. sol. of Cd^{2+}
S''_{12}	$S_1 + S_2$ (6:4) impregnated with 5% aq. sol. of Zn^{2+}
S''_{13}	$S_1 + S_2$ (6:4) impregnated with 5% aq. sol. of Cu^{2+}
S''_{14}	$S_1 + S_2$ (6:4) impregnated with 5% aq. sol. of Cd^{2+}
S''_{15}	$S_1 + S_2$ (4:6) impregnated with 5% aq. sol. of Zn^{2+}
S''_{16}	$S_1 + S_2$ (4:6) impregnated with 5% aq. sol. of Cu^{2+}
S''_{17}	$S_1 + S_2$ (4:6) impregnated with 5% aq. sol. of Cd^{2+}
S''_{18}	$S_1 + S_2$ (2:8) impregnated with 5% aq. sol. of Zn^{2+}
S''_{19}	$S_1 + S_2$ (2:8) impregnated with 5% aq. sol. of Cu^{2+}
S''_{20}	$S_1 + S_2$ (2:8) impregnated with 5% aq. sol. of Cd^{2+}

Table 2.5 Mobile phases used for surfactants

Code	Components
Single component mobile phases	
M_1	Acetone

M_2	Demineralized water (DMW)
Mixed mobile phases	
M_3	$M_1 + M_2$ (9:1)
M_4	$M_1 + M_2$ (8:2)
M_5	$M_1 + M_2$ (7:3)
M_6	$M_1 + M_2$ (6:4)
M_7	$M_1 + M_2$ (5:5)
M_8	$M_1 + M_2$ (4:6)
M_9	$M_1 + M_2$ (3:7)
M_{10}	$M_1 + M_2$ (2:8)
M_{11}	$M_1 + M_2$ (1:9)
M_{12}	$M_1 + M_2$ + DMSO (1:1:1)
M_{13}	$M_1 + M_2$ + DMSO (2:1:1)
M_{14}	$M_1 + M_2$ + DMSO (1:2:1)
M_{15}	$M_1 + M_2$ + DMSO (1:1:2)

Table 2.6 Mobile phases used for metal ions

Code	Components
Single component mobile phases	
M'_1	Demineralized water (DMW)
M'_2	1% aqueous solution of NaCl

Table 2.7 Mobile phases used for pesticides

Code	Components
Single component mobile phase	
M''_1	Acetone
M''_2	0.5% aqueous NaCl
M''_3	1% aqueous NaCl
M''_4	5% aqueous NaCl

M''_5	10% aqueous NaCl
Mixed mobile phases	
M''_6	$M_1 + M_3$ (1:1)
M''_7	$M_1 + M_3$ (3:7)
M''_8	$M_1 + M_3$ (7:3)

PREPARATION OF TLC PLATES

Plain Thin-Layer Plates

TLC Plates were prepared by mixing silica gel G with double distilled water in a 1:3 ratio. The resultant slurry was mechanically shaken for 5 minutes and then it was coated onto glass plates with the help of a TLC applicator to give a layer of 0.25 mm thickness. The plates were first air dried at room temperature and then activated by heating at 100 ± 5 ^{O}C for 1 h. After activation the plates were kept in air tight chamber at room temperature until used.

Soil Thin-Layer Plates

To prepare soil TLC plates, soil sample was slurried mechanically for 5 minutes after mixing with double distilled water in a 1:3 ratio. The resultant homogenous slurry was spread onto 20 x 3.5 cm glass plates as 0.25 mm thick layer. The plates were air dried at room temperature (30 °C) and stored in a air tight chamber at room temperature until used.

Mixed Soil TLC Plates

Soil mixed with silica gel G in different ratios (1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1) by weight were slurried with double distilled water in a 1:3 ratio by shaking for 5 minutes. Using this slurry, thin layers were prepared under the same experimental conditions as described above for plain thin-layer plates.

Impregnated Thin-Layer Plates

TLC plates were prepared by mixing soil or silica or soil + silica ratio with the solution with which the impregnation has to be done (SDS, CTAB and TX-100 in concentrations above and below their CMC values; 5% aqueous solution of copper sulphate, cadmium nitrate and zinc sulphate) in 1:3 ratio and following the same procedure as described above for plain thin-layer plates.

Procedure

About 0.01 ml or 10 µl of test solutions were spotted by means of micropipette about 2.0 cm above the lower edge of the TLC plates. The spots were allowed to dry at room temperature (30 °C). Desired mobile phase was taken in the glass jars and were covered with a lid for about 10 minutes so that the glass jars would get presaturated with mobile phase vapours. Plates were introduced in the jars for the development by ascending technique. Development distance was fixed to 10 cm in all cases. After development the plates were withdrawn from glass jars and dried at room temperature. The spots were detected by using appropriate detectors. The R_L (R_F of leading front) and R_T (R_F of trailing front) values for each spot were determined and the R_F value was calculated as-

$$R_F = \frac{R_L + R_T}{2}$$

For the separation equal volumes of components to be separated were mixed and 10µl of the resultant mixture was spotted on the activated TLC plate which was then dried in air. The plates were developed to a distance of 10 cm, the spots were detected and the separated components were identified on the basis of R_F values.

To study the effect of mobile phase on the separation of various components in a mixture, the separation was carried out by varying mobile phase while

keeping the stationary phase constant. To investigate the effect of nature of stationary phase the mixture was separated on different one component and two component adsorbents keeping mobile phase constant.

For examining the effect of impurities, one drop (5µl) of each the analyte and the impurity solution was spotted successively at the same spot on the line of application of TLC plate. The spot was completely dried after each spotting. After final drying, TLC plate was developed with appropriate mobile phase and the R_F values of the resolved spots were determined.

The limit of detection of agrochemicals was determined by spotting different amounts of analyte on the TLC plates, developing the plates and detecting the spot. The method was repeated with successive lowering of the amount of analyte until no spot was detected. The minimum amount detectable on the TLC plates was taken as the limit of detection.

2.2 RESULTS AND DISCUSSION

The chromatography of surfactants, metal cations and pesticides was performed on different stationary phases using various aqueous mixed-organic solvent systems. The results of entire study have been presented in eighteen Tables (2.8-2.25).

Chromatography of Surfactants:

The mobility pattern of fourteen surfactants (cationic and non ionic) through eleven stationary phases (soil, silica gel and mixed silica-soil) was evaluated using about fifteen mobile phase systems as listed in Table 2.5

Amongst mobile phases investigated, DMW-Acetone-DMSO systems were found favourable in terms of spot compactness and differential migration of surfactants.

The results obtained have been tabulated in Table 2.8 – 2.11. the results reveal the following facts:

1. Detection of surfactants on pure soil bed (S_1) and soil plus silica, 9:1 (S_2) was difficult.
2. Soil added with increasing concentration of silica performs well in terms of clarity in detection and enhancement in mobility.
3. Non-ionic surfactants show higher mobility (R_F range 0.75 – 0.98) compared to the mobility of cationic surfactants (R_F range < 0.3).
4. Tween and Cween produce double spots on certain stationary phases.
5. The mobile phase comprising of Acetone + DWM + DMSO on 1:1:1 volume ratio (M_{12}) was selected for further studies.

Thus, nonionic surfactants can be selectively separated from cationic surfactants. The important separations are listed in Table 2.12.

In order to enhance practical utility of separation, the separation of CPC from the mixture of several nonionic surfactants and the separation of TX–100 from the mixture of cationic surfactants was investigated in the presence of foreign substances (inorganic cations, anionic species, amines and organic dyes). The results are presented in Table 2.13. All the mixtures are well resolved.

The lowest possible amount of surfactants detectable on S_9 (soil + silica, 2:8) was microgram level (Table 2.14). Thus, the proposed method can be applied for sensitive detection and selective separation of cationic and nonionic surfactants on soil containing silica phases.

Chromatography of Metal Ions:

The mobility pattern of eleven heavy metal cations on twenty different stationary phases (soil, silica gel, mixed silica – soil with and without

impregnation) was done using two mobile phases listed in Table 2.6. For impregnation, cationic (CTAB), anionic (SDS) and non-ionic (TX-100) surfactants were used keeping the concentration levels above CMC and below CMC values.

Compared to DMW (M_1'), 1% aq. NaCl solution (M_2') was found more useful in terms of spot detection and differential migration.

In order to understand the migration pattern of heavy metal cations through soil containing silica gel in the presence of surfactants, the stationary phases (soil, silica and soil plus silica) were impregnated with various types of surfactants (cationic, anionic and non anionic) in a wider concentration range (above and below CMC values). The chromatography of metal cations on impregnated phases was performed using DMW and 1% aq. NaCl as mobile phases. The results are presented in Tables 2.15 - 2.17. From the data, following trends are noticeable:

1. Except Mo^{6+}, all metals cations were neatly detected on pure soil bed (S_1). All metals cations give poor mobility on S_1 ($R_F \sim 0.00 - 1.00$) with the exception of Cr^{6+} which migrates to higher distances ($R_F \sim 0.80 - 0.93$) through soil bed.
2. Detection of all the metal cations was very clear on silica or impregnated silica layers (S_2, S9, S10, S11, S12, S13, S14).
3. Except Cr^{6+}, all metal ions are strongly retained on soil compared to other ststionary phases.
4. Zn^{2+}, Fe^{2+}, Fe^{3+} and Cr^{3+} remain near the point of application in all cases.
5. Slight decrease in mobility of all metal cations was observed when soil plus silica, 2:8 (S_{15}, S16, S17, S18, S19, S20) was used as stationary phase instead of silica.

Binary as well as ternary separations are possible on both silica as well as soil plus silica bed. The important separations are listed in Table 2.18. All separations were also performed in presence of interfering species (organic dyes) to examine their effect on separation. All the mixtures are well resolved in the presence of organic dyes.

Chromatography of Pesticides:

The mobility trend of six pesticides through twenty stationary phases (soil, silica gel and mixed silica soil - with and without impregnation) was evaluated using about eight mobile systems as given in Table 2.7. For impregnation 5% aq. salt solution of Cu, Zn and Cd were used.

Amongst the mobile phases investigated, acetone + aq. NaCl systems (M_6'', M_7'', M_8'') were found favourable in terms of spot compactness, detection and differential migration of pesticides.

The results obtained have been tabulated in Table 2.21 – 2.24. The results reveal the following facts:

1. Except ziram, other pesticides were clearly detected on pure soil bed (S_1). Methyl parathion, malathion and dichlorovos show tailed spots ($R_F > 0.3$). Chloropyrifos gives zero mobility on soil.
2. All the six pesticides were clearly detected when pure silica (S_2) was used as stationary phase. Higher mobility for pesticides on silica was observed as compared to their mobility on soil. Chloropyrifos was found to remain close to the point of application on silica and soil layers.
3. Though ziram was easily detected on pure silica but it could not be on metal ion (Cu, Zn and Cd) impregnated plates.
4. Detection of spots on Cd impregnated TLC layers was found somewhat difficult as compared to Cu and Zn impregnated layers.

5. Soil added with increasing concentration of silica performs well in terms of clarity of detection and enhancement in mobility.
6. Soil plus silica, 8:2 (S_6'', S_7'', S_8'') as stationary phase and acetone + 1% aq. NaCl sol. (1:1, vol. / vol.) as mobile phase were chosen for further studies.

Many binary separations are possible. The important separations are listed in Table 2.25.

Table 2.8 R_F values of surfactants obtained on different stationary phases using M_{12} mobile phase

Surfactant	Stationary phase (R_F values)										
	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}
TX-100	ND	0.93	0.87	0.85	0.91	0.76	0.92	0.92	0.90	0.91	0.94
BJ-35	0.98	0.97	0.92	0.95	0.96	0.94	0.98	0.94	0.97	0.96	0.95
BJ-57	0.92	ND	ND	0.73	0.85	0.88	0.84	0.93	0.84	0.89	0.90
BJ-78	ND	ND	ND	0.70	0.82	0.90	0.85	0.91	0.85	0.79	0.88
BJ-98	0.91	0.96	0.80	0.80	0.83	0.91	0.80	0.89	0.86	0.86	0.89
TW-20	ND	ND	0.96	0.97	0.97	0.98	0.98	0.99	0.96	DS	0.97
CW-20	ND	0.95	0.93	0.91	DS	0.95	0.96	0.95	0.92	DS	0.95
CW-40	ND	0.94	0.89	0.91	0.89	0.82	0.95	DS	0.96	DS	0.87
CW-60	ND	0.91	0.97	0.95	0.93	0.95	0.95	DS	0.97	DS	DS
CPC	0.04	0.00	0.04	0.06	0.15	0.09	0.07	0.21	0.10	0.18	0.10
CTAB	0.04	0.00	0.03	0.05	0.10	0.07	0.05	0.19	0.12	0.11	0.12
TTAB	0.13	0.08	0.17	0.12	0.16	0.06	0.12	0.20	0.12	0.18	0.25
HDTAC	ND	ND	0.04	0.08	0.10	0.05	0.08	0.15	0.06	0.26	0.13
DTAB	ND	ND	0.15	0.30	0.26	0.17	0.21	0.30	0.31	0.33	0.30

ND = Not detected

DS = Double Spots (R_F 0.00 and R_F 0.94)

Table 2.9 R_F values of surfactants obtained on different stationary phases using M_{13} mobile phase

Surfactant	Stationary phase (R_F values)										
	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}
TX-100	0.70	0.94	0.89	0.86	0.92	0.93	0.95	0.95	0.93	0.98	0.97
BJ-35	0.96	0.98	0.93	0.96	0.96	0.90	0.97	0.93	0.91	0.97	0.96
BJ-57	0.92	0.89	0.91	0.81	0.89	0.91	0.80	0.89	0.90	0.93	0.89
BJ-78	0.97	0.87	0.97	0.79	0.85	0.90	0.81	0.87	0.89	0.95	0.90
BJ-98	ND	0.97	0.80	0.75	0.84	0.90	0.83	0.93	0.94	0.93	0.89
TW-20	ND	ND	0.82	0.82	0.98	0.95	0.99	0.98	0.96	DS	0.96
CW-20	0.98	0.96	0.98	0.97	0.96	0.85	0.97	0.96	0.95	0.97	0.93
CW-40	ND	0.95	0.90	0.91	0.91	0.89	0.96	0.95	0.93	DS	0.83
CW-60	0.94	0.92	0.98	0.96	0.95	0.91	0.89	0.93	0.92	0.97	0.86
CPC	0.14	0.50	0.05	0.07	0.23	0.16	0.09	0.25	0.20	0.16	0.41
CTAB	ND	0.40	0.04	0.06	0.22	0.24	0.04	0.16	0.07	0.09	0.22
TTAB	0.17	0.09	0.20	0.18	0.25	0.32	0.05	0.08	0.20	0.21	0.18
HDTAC	ND	ND	0.05	0.10	0.22	0.19	0.11	0.19	0.34	0.19	0.14
DTAB	ND	ND	0.17	0.33	0.30	0.10	0.20	0.29	0.35	0.32	0.35

ND = Not detected

DS = Double spots (R_F 0.00 and R_F 0.97)

Table 2.10 R_F values of surfactants obtained on different stationary phases using M_{14} mobile phase

Surfactant	Stationary phase (R_F values)										
	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}
TX-100	ND	0.85	0.84	0.85	0.84	0.76	0.89	0.87	0.81	0.91	0.86
BJ-35	ND	0.84	0.86	0.83	0.83	0.87	0.89	0.98	0.97	0.96	0.96
BJ-57	0.61	0.82	0.80	0.81	0.84	0.88	0.84	0.92	0.65	0.91	0.88
BJ-78	ND	0.80	0.79	0.80	0.83	0.89	0.85	0.89	0.96	0.92	0.90
BJ-98	ND	0.75	0.79	0.80	0.81	0.60	0.60	0.67	0.63	0.84	0.76
TW-20	ND	ND	0.97	0.96	0.92	0.65	0.65	0.98	0.93	0.93	0.93
CW-20	ND	0.76	0.77	0.79	0.75	DS	0.77	0.94	DS	DS	0.86
CW-40	0.97	0.95	0.91	0.92	0.91	0.92	0.93	DS	DS	DS	DS
CW-60	ND	0.72	0.75	0.80	0.81	DS	0.82	0.98	DS	0.97	DS
CPC	0.00	0.02	0.04	0.05	0.05	0.04	0.05	0.04	0.02	0.08	0.05
CTAB	0.00	0.04	0.04	0.06	0.05	0.06	0.06	0.04	0.03	0.04	0.05
TTAB	0.17	0.08	0.08	0.07	0.08	0.09	0.08	0.08	0.06	0.15	0.11
HDTAC	0.00	ND	0.04	0.07	0.10	0.04	0.089	0.02	0.03	0.00	0.03
DTAB	ND	ND	0.20	0.31	0.21	0.18	0.23	0.16	0.16	0.19	0.28

ND = Not detected

DS = Double spots (R_F 0.00 and R_F 0.92)

Table 2.11 R_F values of surfactants obtained on different stationary phases using M_{15} mobile phase

Surfactant	Stationary phase (R_F values)										
	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}
TX-100	ND	0.92	0.93	0.93	0.92	0.91	0.93	0.92	0.96	0.93	0.95
BJ-35	0.98	0.97	0.96	0.96	0.95	0.98	0.97	0.96	0.97	0.96	0.96
BJ-57	0.75	0.77	0.72	0.79	0.82	0.83	0.89	0.90	0.92	091	0.91
BJ-78	0.70	0.72	0.72	0.73	0.82	0.75	0.79	0.92	0.92	0.97	0.83
BJ-98	ND	0.76	0.79	0.80	0.74	0.73	0.83	0.90	0.86	0.87	0.91
TW-20	ND	ND	0.95	0.96	0.96	0.97	0.96	0.98	0.99	0.98	0.96
CW-20	ND	0.91	0.91	0.93	0.94	0.95	0.95	0.94	0.97	DS	0.95
CW-40	ND	0.91	0.91	0.93	0.92	0.93	0.92	0.94	0.93	DS	0.91
CW-60	ND	0.96	0.97	0.97	0.95	0.97	0.96	0.97	0.95	0.94	0.96
CPC	0.12	0.19	0.20	0.21	0.18	0.18	0.19	0.21	0.21	0.21	0.33
CTAB	0.20	0.19	0.20	0.19	0.18	0.20	0.20	0.11	0.17	0.21	0.24
TTAB	0.25	0.19	0.19	0.29	0.27	0.25	0.21	0.13	0.20	0.43	0.20
HDTAC	ND	ND	0.18	0.17	0.16	0.19	0.19	0.08	0.15	0.29	0.11
DTAB	ND	ND	0.30	0.25	0.32	0.35	0.30	0.12	0.47	0.23	0.28

ND = Not detected

DS = Double spots (R_F 0.00 and R_F 0.96)

Table 2.12 Experimentally achieved separations of surfactants on soil mixed with silica gel layer (S_9) developed with mobile phase acetone + DMW + DMSO (1:1:1 M_{12})

Mixture of Surfactant	Separation (R_F values)
BJ-35 + CTAB	BJ-35 (0.97) - CTAB (0.16)
BJ-35 + HDTAC	BJ-35 (0.96) - HDTAC (0.11)
BJ-57 + TTAB	BJ-57 (0.78) - TTAB (0.17)
BJ-57 + DTAB	BJ-57 (0.79) - DTAB (0.17)
BJ-78 + DTAB	BJ-78 (0.82) - DTAB (0.26)
BJ-78 + HDTAC	BJ-78 (0.83) - HDTAC (0.09)
BJ-98 + CTAB	BJ-98 (0.83) - CTAB (0.12)
TX-100 + CPC	TX-100 (0.94) - CPC (0.15)
TX-100 + DTAB	TX-100 (0.94) - DTAB (0.23)
Mix^a + CPC	Mix^a (0.87) - CPC (0.11)
Mix^a + CTAB	Mix^a (0.88) - CTAB (0.12)
Mix^a + TTAB	Mix^a (0.90) - TTAB (0.17)
Mix^a + HDTAC	Mix^a (0.90) - HDTAC (0.08)
Mix^a + DTAB	Mix^a (0.88) - DTAB (0.19)
Mix^b + TX-100	Mix^b (0.16, T) TX-100 (0.89)
Mix^b + BJ-35	Mix^b (0.17, T) - BJ-35 (0.97)
Mix^b + BJ-57	Mix^b (0.15) - BJ-57 (0.77)
Mix^b + BJ-78	Mix^b (0.17, T) - BJ-78 (0.90)
Mix^b + BJ-98	Mix^b (0.18, T) - BJ-98 (0.86)

Mix^a - Mixture of five nonionic surfactants (TX-100 + BJ-35 + BJ-57 + BJ- 78 + BJ-98)

Mix^b - Mixture of five cationic surfactants (CPC + CTAB + TTAB + HDTAC + DTAB)

T - Tailed spot ($R_L - R_T \geq 0.3$)

Table 2.13 Effect of foreign species on the separation efficiency of surfactants

Interfering species	Separation (R_F values)			
	Mix[a] + CPC		Mix[b] + TX-100	
Metal Cations				
Tl^{3+}	0.82	0.12	0.14	0.92
Th^{2+}	0.83	0.14	0.12	0.89
Zn^{2+}	0.85	0.14	0.15	0.93
Cu^{2+}	0.86	0.11	0.16 (T)	0.89
Hg^{2+}	0.79	0.04	0.11	0.89
Pb^{2+}	0.92	0.05	0.07	0.91
Anions				
SO_4^{2-}	0.91	0.06	0.06	0.91
NO_3^{2-}	0.89	0.04	0.06	0.91
SCN^-	0.89	0.03	0.05	0.91
Cl^-	0.91	0.05	0.05	0.91
Amines				
L-Naphthyl amine	0.86	0.02	0.03	0.92
Methyl amine	0.86	0.04	0.05	0.90
Tributyl amine	0.83	0.07	0.05	0.92
Tetrabutyl amine	0.89	0.00	0.05	0.93
Diphenyl amine	0.84	0.03	0.05	0.86
Organic Dyes				
Bromocresol green	0.88	0.05	0.06	0.93
Ammonium purpurate	0.89	0.04	0.07	0.93
Thorin indicator	0.88	0.04	0.06	0.94
Bromocresol purple	0.77 (T)	0.03	0.06	0.94
Methyl red	0.91	0.05	0.06	0.94

T - Tailed spot ($RL - RT \geq 0.3$)

Table 2.14 Limit of detection of various surfactants studied

Surfactant	Limit of Detection (μg)
TX-100	0.5
BJ-35	0.15
BJ-57	0.5
BJ-78	0.5
BJ-98	9.0
CPC	0.15
CTAB	2.0
TTAB	0.5
HDTAC	0.8
DTAB	0.8

Table 2.15 R_F values of metal cations on soil layers impregnated with surfactants (above and below CMC value) using water and aqueous sodium chloride solution as mobile phases

Metal Ion	Stationary phase : Soil Impregnated with		
	TX-100	CTAB	SDS
Mobile Phase : DMW			
Zn^{2+}	0.00* (0.00)	0.01* (0.00)	0.02* (0.00)
Cd^{2+}	0.02 (0.02)	0.04 (0.02)	0.02 (0.02)
Ni^{2+}	0.01 (0.00)	0.03 (0.00)	0.03 (0.02)
Co^{2+}	0.03 (0.00)	0.03 (0.00)	0.02 (0.03)
Mo^{6+}	ND (ND)	ND (ND)	ND (ND)
Cu^{2+}	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Fe^{2+}	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Fe^{3+}	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Cr^{3+}	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Cr^{6+}	0.92 (0.93)	0.85 (0.84)	0.79 (0.91)
Mn^{2+}	0.00 (0.00)	0.02 (0.00)	0.03 (0.02)
Mobile Phase : 1% aqueous sol. of NaCl			
Zn^{2+}	0.03 (0.04)	0.02 (0.03)	0.02 (0.02)
Cd^{2+}	0.08 (0.13)	0.08 (0.07)	0.08 (0.10)
Ni^{2+}	0.06 (0.05)	0.07 (0.05)	0.06 (0.06)
Co^{2+}	0.07 (0.08)	0.07 (0.06)	0.05 (0.08)
Mo^{6+}	ND (ND)	ND (ND)	ND (ND)
Cu^{2+}	0.02 (0.03)	0.02 (0.00)	0.00 (0.02)
Fe^{2+}	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Fe^{3+}	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Cr^{3+}	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Cr^{6+}	0.81, T (0.93)	0.01 (0.83)	0.90 (0.90)
Mn^{2+}	0.06 (0.07)	0.07 (0.05)	0.04 (0.80)

* R_F values obtained on impregnated layers with surfactant above their CMC value. The values within bracket are those obtained on surfactant impregnated layer below CMC value.

ND = Not detected

T = Tailed spot (RL – RT > 0.3)

Table 2.16 R_F values of metal cations on soil plus silica (2:8) layers impregnated with surfactants (above and below CMC value) using water and aqueous sodium chloride solution as mobile phase

Metal Ion	Stationary Phase : Soil + Silica (2:8) impregnated with surfactants		
	TX-100	CTAB	SDS
Mobile phase : DMW			
Zn^{2+}	0.04* (0.03)	0.06* (0.06)	0.04* (0.04)
Cd^{2+}	0.26, T (0.25, T)	0.28, T (0.26, T)	0.37, T (0.44, T)
Ni^{2+}	0.49 (0.47)	0.50, T (0.38, T)	0.30 (0.31)
Co^{2+}	0.33 (0.28)	0.37 (0.32)	0.26 (0.28)
Mo^{6+}	0.97 (0.96)	0.95 (0.97)	0.83, T (0.97)
Cu^{2+}	0.04 (0.03)	0.07 (0.04)	0.06 (0.09)
Fe^{2+}	0.02 (0.02)	0.04 (0.03)	0.02 (0.02)
Fe^{3+}	0.02 (0.01)	0.00 (0.00)	0.00 (0.00)
Cr^{3+}	0.02 (0.02)	0.00 (0.00)	0.05 (0.00)
Cr^{6+}	0.92 (0.92)	0.95 (0.94)	0.95 (0.95)
Mn^{2+}	0.33 (0.27)	0.25, T (0.23, T)	0.05, T (0.33, T)
Mobile phase : 1% aqueous sol. of NaCl			
Zn^{2+}	0.05 (0.04)	0.05 (0.06)	0.04 (0.05)
Cd^{2+}	0.45, T (0.47, T)	0.35, T (0.48, T)	0.72, T (0.47, T)
Ni^{2+}	0.53, T (0.54)	0.65, T (0.62, T)	0.35 (0.55)
Co^{2+}	0.43 (0.41)	0.40, T (0.45, T)	0.43, T (0.52, T)
Mo^{6+}	0.97 (0.97)	0.95 (0.97)	0.78, T (0.95)
Cu^{2+}	0.05 (0.04)	0.04 (0.05)	0.09 (0.13)
Fe^{2+}	0.02 (0.02)	0.02 (0.02)	0.01 (0.02)
Fe^{3+}	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Cr^{3+}	0.00 (0.00)	0.00 (0.00)	0.07 (0.00)
Cr^{6+}	0.92 (0.92)	0.92 (0.95)	0.90 (0.90)
Mn^{2+}	0.59 (0.56)	0.60 (0.62)	0.05 (0.43, T)

* RF values obtained on impregnated layers with surfactant above their CMC value. The values within bracket are those obtained on surfactant impregnated layer below CMC value

T - Tailed spot ($R_L - R_T > 0.3$)

Table 2.17 R_F values of metal cations on silica layers impregnated with surfactants (above and below CMC value) using water and aqueous sodium chloride solution as mobile phases

Metal Ion	Stationary phase : Silica Impregnated with surfactants		
	TX-100	CTAB	SDS
Mobile Phase : DMW			
Zn^{2+}	0.08* (0.07)	0.13* (0.10)	0.07* (0.06)
Cd^{2+}	0.67, T (0.68, T)	0.67, T (0.75, T)	0.34, T (0.27, T)
Ni^{2+}	0.83, T (0.77, T)	0.93 (0.89)	0.68, T (0.71, T)
Co^{2+}	0.87 (0.80, T)	0.9 (0.87)	0.71, T (0.61, T)
Mo^{6+}	0.97 (0.95)	0.92 (0.97)	0.92 (0.96)
Cu^{2+}	0.31, T (0.18, T)	0.29, T (0.22, T)	0.05 (0.07)
Fe^{2+}	0.04 (0.04)	0.07 (0.07)	0.05 (0.05)
Fe^{3+}	0.03 (0.03)	0.04 (0.05)	0.05 (0.05)
Cr^{3+}	0.04 (0.04)	0.05 (0.04)	0.03 (0.06)
Cr^{6+}	0.95 (0.96)	0.95 (0.95)	0.94 (0.95)
Mn^{2+}	0.90 (0.84, T)	0.85, T (0.81, T)	0.78 (0.82)
Mobile phase : 1% aqueous sol. of NaCl			
Zn^{2+}	0.14 (0.15, T)	0.13 (0.13)	0.08 (0.09)
Cd^{2+}	0.98 (0.98)	0.71 (0.96)	0.87 (0.90)
Ni^{2+}	0.95 (0.95)	0.96 (0.97)	0.93 (0.91)
Co^{2+}	0.96 (0.95)	0.94 (0.97)	0.92 (0.86)
Mo^{6+}	0.91 (0.95)	0.93 (0.97)	0.94 (0.87)
Cu^{2+}	0.32, T (0.34, T)	0.28, T (0.23, T)	0.10 (0.10)
Fe^{2+}	0.05 (0.06)	0.07 (0.07)	0.05 (0.06)
Fe^{3+}	0.02 (0.04)	0.05 (0.05)	0.06 (0.07)
Cr^{3+}	0.07 (0.02)	0.04 (0.02)	0.06 (0.05)
Cr^{6+}	0.96 (0.97)	0.95 (0.96)	0.95 (0.95)
Mn^{2+}	0.93 (0.96)	0.95 (0.95)	0.47 (0.49, T)

* RF values obtained on impregnated layers with surfactant above their CMC value. The values within bracket are those obtained on surfactant impregnated layer below CMC value

T - Tailed spot ($R_L - R_T > 0.3$)

Table 2.18 Experimentally achieved separation of metal cations on soil plus silica (2:8) layers impregnated with TX-100 and CTAB below their CMC value using 1% aq. NaCl sol. as mobile phase

Plates Impregnated with TX-100 (↓CMC)	
Mixture	**Separation (R_F values)**
$Zn^{2+} + Mn^{2+}$	Zn^{2+} (0.04) - Mn^{2+} (0.47)
$Zn^{2+} + Co^{2+}$	Zn^{2+} (0.04) - Co^{2+} (0.40, T)
$Mn^{2+} + Cu^{2+}$	Mn^{2+} (0.46) - Cu^{2+} (0.04)
$Cu^{2+} + Co^{2+} + Mo^{6+}$	Cu^{2+} (0.03) - Co^{2+} (0.40) - Mo^{6+} (0.97)
$Zn^{2+} + Ni^{2+} + Mo^{6+}$	Zn^{2+} (0.04) - Ni^{2+} (0.54) - Mo^{6+} (0.97)
Plates Impregnated with CTAB (↓CMC)	
Mixture	**Separation (R_F values)**
$Zn^{2+} + Ni^{2+}$	Zn^{2+} (0.06) - Ni^{2+} (0.62, T)
$Fe^{2+} + Ni^{2+}$	Fe^{2+} (0.02) - Ni^{2+} (0.62, T)
$Cu^{2+} + Co^{2+}$	Cu^{2+} (0.05) - Co^{2+} (0.45, T)
$Mo^{6+} + Mn^{2+} + Fe^{2+}$	$Mo6^{+}$ (0.97) - Mn^{2+} (0.43) - Fe^{2+} (0.00)
$Zn^{2+} + Ni^{2+} + Mo^{6+}$	Zn^{2+} (0.04) - Ni^{2+} (0.42) - Mo^{6+} (0.97)

T = Tailed spot ($R_L - R_T > 0.3$)

Table 2.19 Experimentally achieved separations of metal cations on silica layers impregnated with TX-100 and CTAB below their CMC value using 1% aq. NaCl sol. as mobile phase

(i) Plates Impregnated with TX-100	
Mixture	**Separation (R_F values)**
$Zn^{2+} + Mn^{2+}$	Zn^{2+} (0.15, T) - Mn^{2+} (0.97)
$Zn^{2+} + Cd^{2+}$	Zn^{2+} (0.13) - Cd^{2+} (0.98)
$Cu^{2+} + Cd^{2+}$	Cu^{2+} (0.25, T) - Cd^{2+} (0.97)
$Fe^{3+} + Ni^{2+}$	Fe^{3+} (0.03) - Ni^{2+} (0.95)
(ii) Plates Impregnated with CTAB	
Mixture	**Separation (R_F values)**
$Cu^{2+} + Cd^{2+}$	Cu^{2+} (0.28, T) - Cd^{2+} (0.95)
$Cu^{2+} + Mn^{2+}$	Cu^{2+} (0.23) - Mn^{2+} (0.95)
$Zn^{2+} + Cd^{2+}$	Zn^{2+} (0.13) - Cd^{2+} (0.96)
$Zn^{2+} + Mo^{6+}$	Zn^{2+} (0.12) - Mo^{6+} (0.97)

T = Tailed spot ($R_L - R_T > 0.3$)

...soil plus silica stationary bed impregnated with TX-100 ...esence of organic dyes as impurities with 1% aqueous NaCl

...ase	Interfering Species	Mixture for Analysis	Separation (R_F values)
...il + Silica (2:8) ...mpregnated with TX-100	Aluminone Patent blue	$Zn^{2+} + Mn^{2+}$ $Cu^{2+} + Co^{2+} + Mo^{6+}$	Zn^{2+} (0.04) – Mn^{2+} (0.43) Cu^{2+} (0.03) – Co^{2+} (0.48, T) – Mo^{6+} (0.97)
Soil + Silica (2:8) Impregnated with CTAB	Congo red Methyl red	$Cu^{2+} + Co^{2+}$ $Zn^{2+} + Ni^{2+} + Mo^{6+}$	Cu^{2+} (0.04) – Co^{2+} (0.49, T) Zn^{2+} (0.03) – Ni^{2+} (0.52, T) – Mo^{6+} (0.97)
Silica Impregnated with TX-100	Brilliant green Alizarin red S	$Zn^{2+} + Cd^{2+}$ $Cu^{2+} + Cd^{2+}$	Zn^{2+} (0.09) – Cd^{2+} (0.91) Cu^{2+} (0.11) – Cd^{2+} (0.90)
Silica impregnated with CTAB	Bromo cresol purple Saffranine	$Zn^{2+} + Mo^{6+}$ $Mn^{2+} + Cu^{2+}$	Zn^{2+} (0.08) – Mo^{6+} (0.96) Mn^{2+} (0.85) – Cu^{2+} (0.07)

Table 2.21 R_F values of pesticides on soil TLC plates impregnated with 1% aq. $CuSO_4$ solution using different mobile phases

Pesticide	Mobile phase (R_F)				
	M_1''	M_2''	M_3''	M_4''	M_5''
MLPN	0.85	0.70 (T)	0.72 (T)	0.00	0.67
MLN	0.75 (T)	0.69 (T)	0.52 (T)	0.00	0.00
DCVS	0.75 (T)	0.10	0.00	0.00	0.00
DMT	0.83	0.65 (T)	0.65	0.60	0.61
CPS	0.17 (T)	0.11	0.00	0.17 (T)	0.3 (T)
ZRM	ND	ND	ND	ND	ND

ND = Not detected

T = Tailed spots ($R_L - R_T > 0.3$)

Table 2.22 R_F values of pesticides on soil TLC plates impregnatged with 1% aq. salt solution of Cu, Zn and Cd using different mobile phases

Pesticide	Mobile phase								
	M_6''			M_7''			M_8''		
	Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd
MLPN	0.62 (T)	0.78	0.67	0.86	0.81	0.68	0.79	0.73	0.67
MLN	0.73 (T)	0.60 (T)	0.52 (T)	0.77	0.86	0.60	0.57 (T)	0.59 (T)	0.39 (T)
DCVS	0.59 (T)	0.38	0.53 (T)	0.55	0.70 (T)	0.35 (T)	0.00	0.00	0.00
DMT	0.60 (T)	0.68	0.72	0.77	0.84	0.76	0.71 (T)	0.72 (T)	0.66 (T)
CPS	0.29 (T)	0.50	0.28 (T)	0.56	0.68 (T)	0.64	0.88	0.15 (T)	0.34 (T)
ZRM	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = Not detected

T = Tailed spot ($R_L - R_T > 0.3$)

Table 2.23 Mobility of pesticides on pure soil (S_1) and pure silica (S_2) layers using acetone + 1% aq. NaCl sol., 1:1 vol./vol. (M_6'') as mobile phase

Pesticide	Soil	Silica
MLPN	0.76 (T)	0.83
MLN	0.59 (T)	0.74
DCVS	0.50 (T)	0.76
DMT	0.80	0.67
CPS	0.00	0.02
ZRM	ND	0.00

ND = Not detected

T = Tailed spot ($R_L - R_T > 0.3$)

Table 2.24 R_F values of pesticides on Soil, Soil + Silica and Silica layers impregnated with 5% aq. solution of Cu, Zn and Cd salts using Acetone + 1% aq. NaCl sol., 1:1 vol./vol. (M_6'') as mobile phase

Pesticide	Soil			8:2			6:4			4:6			2:8			Silica		
	Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd
MLPN	0.47 (T)	0.07	0.09	0.81	0.88	0.57	0.74	0.88	0.64	0.78	0.90	0.61	0.72	0.86	0.62	0.79	0.66	0.70
MLN	0.45 (T)	0.33	0.35 (T)	0.68	0.75	0.54	0.67	0.81	0.56 (T)	0.68	0.80	0.60	0.75	0.77 (T)	0.53	0.60 (T)	0.78	0.52
DCVS	0.46 (T)	0.43	0.42 (T)	0.63	0.60	0.30 (T)	0.66	0.60	0.54	0.60	0.72	0.53	0.67	0.41	0.59	0.65	0.40	0.67
DMT	0.68	0.77	0.30 (T)	0.68	0.82	0.60	0.68	0.66 (T)	0.46 (T)	0.74	0.80	0.58	0.79	0.85	0.61	0.74	0.21 (T)	0.40
CPS	0.18 (T)	0.07	0.19 (T)	0.04	0.06	0.02	0.08	0.23	0.04	0.04	0.07	0.04	0.13	0.09	0.02	0.22	0.00	0.07
ZRM	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = Not detecdted

T = Tailed spot ($R_L - R_T > 0.3$)

Table 2.25 Experimentally achieved separations of pesticides on soil plus silica layers impregnated with 5% aq. salt sol. of Cu, Zn and Cd using acetone + 1% aq. NaCl (1:1, vol./vol.) as mobile phase

Mixture	Separation (R_F values)
(i) Cu Impregnation	
CPS + DMT	CPS (0.03) – DMT (0.64)
CPS + MLPN	CPS (0.02) – MLPN (0.61)
CPS + DCVS	CPS (0.06) – DCVS (0.59)
(ii) Zn Impregnation	
CPS + DMT	CPS (0.07) – DMT (0.69)
CPS + MLPN	CPS (0.12) – MLPN (0.78)
CPS + MLN	CPS (0.20) – MLN (0.68)
(iii) Cd Impregnation	
CPS + DMT	CPS (0.06) – DMT (0.47)
CPS + MLN	CPS (0.06) – MLN (0.35)

References

1. J. Sherma, *Anal. Chem.*, 2000, **72**, 9R.
2. J. Sherma, *Anal. Chem.*, 1998, **70**, 7R.
3. J. Sherma, *Anal. Chem.*, 1996, **68**, 1R.
4. J. Sherma and B. Fried, "*Handbook of Thin-Layer Chromatography*", *Marcel Dekker, New York,* 4th. Edu. 1999.
5. A. Mohammad, M. Ajmal, S. Anwar and E. Iraqi, *J. Planar Chroamtogr. –Mod. TLC*, 1996, **6,** 318.
6. A. Mohammad, N. Fatima, J. Ahmad and M. A. M. Khan, *J. Chromatogr.*, 1993, **642,** 445.
7. J. Sherma, *J. Planar Chromatogr. –Mod. TLC,* 1994, **7**, 265.
8. H. S. Rathore and T. Begum, *J. Chromatogr.*, 1993, **643**, 271.
9. A. Mohammad and S. Anwar in "Industry Environment and Pollution", P. K. Goyal and A. Kumar (eds.) *ABD publishers, Jaipur (India)* 2000, 377.
10. K. D. Rana, B. D. Mali and M. V. Garad. *J. Planar Chromatogr.–Mod. TLC*, 1997, **10**, 220.
11. M. Petrovic, S. Babic and M. S. Kastelan-Macan, *Croat. Chem. Acta,* 2000, **73**, 197.
12. V. B. Patil, M. T. Sevalkar and S. V. Padalikar, *Analyst,* 1992**, 72,** 75.
13. K. Fodor-(sorba in J. Sherma and B. Fried Leds.) "*Handbook of Thin-Layer Chromatogrraphy*", Marcel Dekker, New York 2nd edn. 1996, 753.
14. R. Carson, "Silent Spring", Faw cett publishers, *Inc. Greenwish Cenn.* 1970.

15. B. J. Walker, "Organophosphorus Chemistry", *Penguin Books, Austraila, Ltd. Australia*, 1972.

16. C. A. Edwards, "Environmental Pollution by Pesticides", 1973, **3**, 1, 204, 421, 451, 467, *Plenum Press, London.*

17. A. S. Atwal, "Agricultural Pests of India and South East Asia", *Kalyani Publishers, Delhi*, 1976.

18. K. G. Das, "Pesticides Analysis", *Marcel Dekkar, New York* 1981.

19. D. Bull, "A growing problem-The Pesticide and Third World Poor", *OXFAM*, 1982.

20. J. H. A. Ruzicka and D. C. Abbott, "Pesticide residue analysis", *Talanta,* 1973, **20**, 1261.

21. "Pesticide Analytical Manual, Methods for Individual Pesticide Residue", 2, Food and Drug Administration, Bureau of foods, Washington D.C., U.S.A., 1978.

22. "International conference on pesticide toxicity, safety and risk assessment", soibsired by council of scientific and Industrial Research, New Delhi, I.T.R.C. Lucknow, India, 27th-31st October-1985.

23. J. R. Kruger, R. G. Butz and D. J. Cork, *J. Agric. Food. Chem.*, 1991, **39**, 995.

24. H. T. Crisanto and L. F. Martin, *Toxicol. Environ. Chem.*, 1991, **31-32,** 63.

25. V. F. Gruber, B. A. Halley, S. C. Hwang and C. C. Ku, *J. Agric. Food Chem.*, 1990, **38**, 886.

26. W. Dedek, R. Grahi and B. Methes, *J. Chromatogr.* 1985, **331**, 200.

27. J. Sherma, H. D. Harwett and A. V. Jain, *J. Liq. Chromatogr. Relat. Technol.*, 1999, **22**, 137.

28. C. S. Helling and B. C. Turner, *Science*, 1968, **162**, 562.

29. S. U. Khan and N. N. Khan., *Soil Science*, 1986, **142**, 214

30. C. S. Helling, *Soil Sci. Soc. An. Proc.*, 1971, **35**, 743, 732, 737.

31. P. Jamet and J. C. Thoisy-Dur, *Bull. Environ. Contam. Toxicol.*, 1998, **41**, 135.

32. C. R. Rhodes, I. J. Belasco and H. L. Pease, *J. Agric. Food Chem.* 1990, **18**, 524.

33. J. P. Singhal and R. P. Singh, *Colloid. Polym. Sci:*, 1977, **255**, 488.

34. S. U. Khan, M. A. Qureshi and J. B. Singh, *Indian J. Environ. Health*, 1996, **38**, 1.

35. S. U. Khan, R. K. Bhardwaj, S Jabin and J. A. Khan, *Poll. Res.*, 2000, **19**, 241.

36. E. Stahl, "Thin-Layer Chromatography "*(Springer, Berlin)* 1996.

37. J. P. Singhal, S. U. Khan and V. Bansal, *Proc. Of the Indian National Science Academy*, 1978, **44**, 267.

38. S. U. Khan, T. Begum and J. Singh, *Indian J. Environ. Health*, 1996, **38**, 41.

39. M. Sanchez-Canazono and M. J. Sanchez-Martin, *J. Chromatogr.*, 1993, **643**, 35